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Itoh et al.

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(54) METHOD FOR GROWING NITRIDE SEMICONDUCTOR CRYSTALS, NITRIDE SEMICONDUCTOR DEVICE, AND METHOD FOR FABRICATING THE SAME

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(22) Filed: **May 25, 1999**

(30) Foreign Application Priority Data

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(51) **Int. Cl.**^{7} **H01L 21/00**

(52) **U.S. Cl.** **438/46**; 438/22; 438/47; 438/765; 438/775

(58) **Field of Search** 438/22, 46, 42, 438/765, 775

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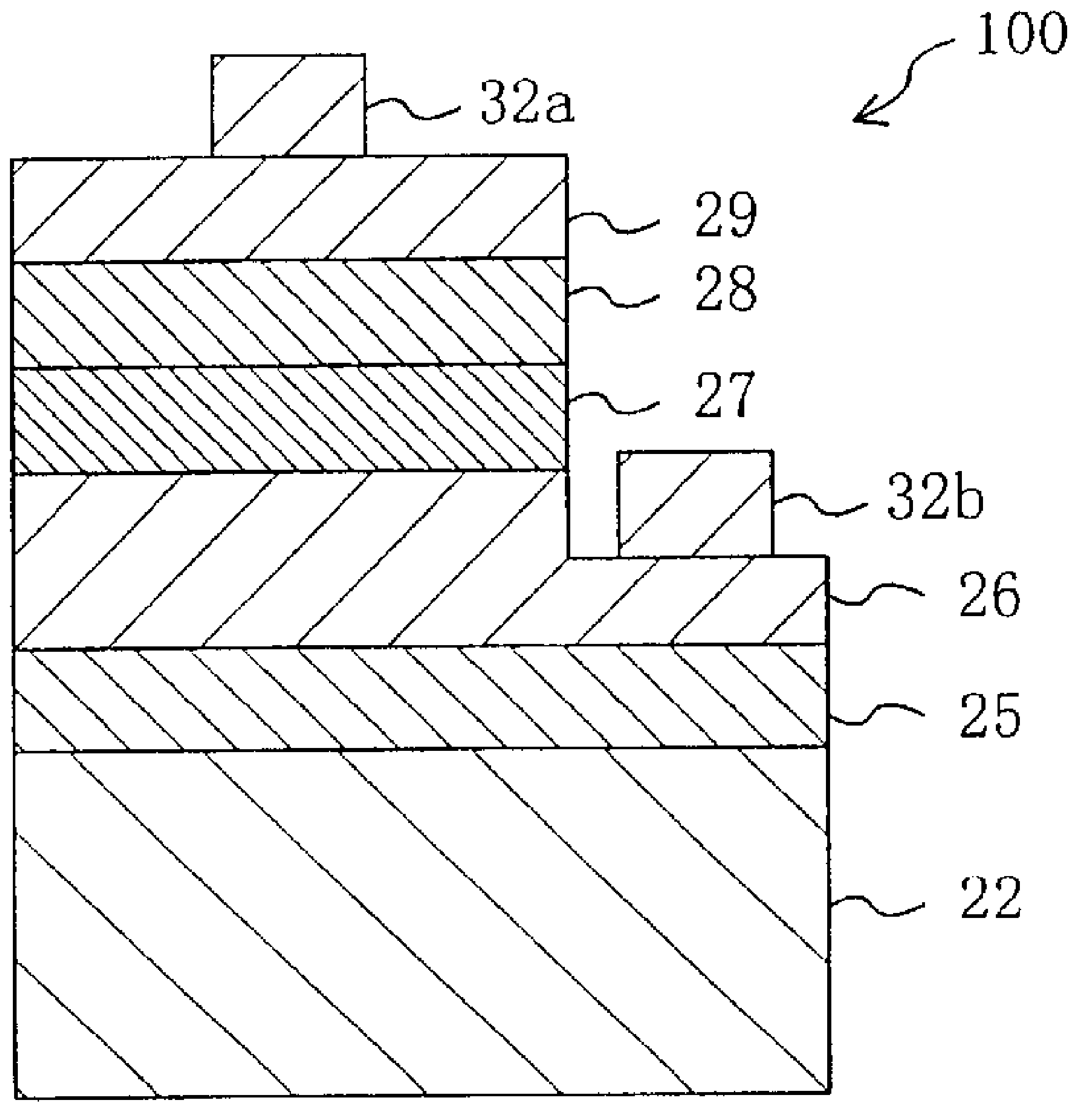
(57) ABSTRACT

A method for growing nitride semiconductor crystals according to the present invention includes the steps of: a) forming a first metal single crystal layer on a substrate; b) forming a metal nitride single crystal layer by nitrifying the first metal single crystal layer; and c) epitaxially growing a first nitride semiconductor layer on the metal nitride single crystal layer.

13 Claims, 14 Drawing Sheets



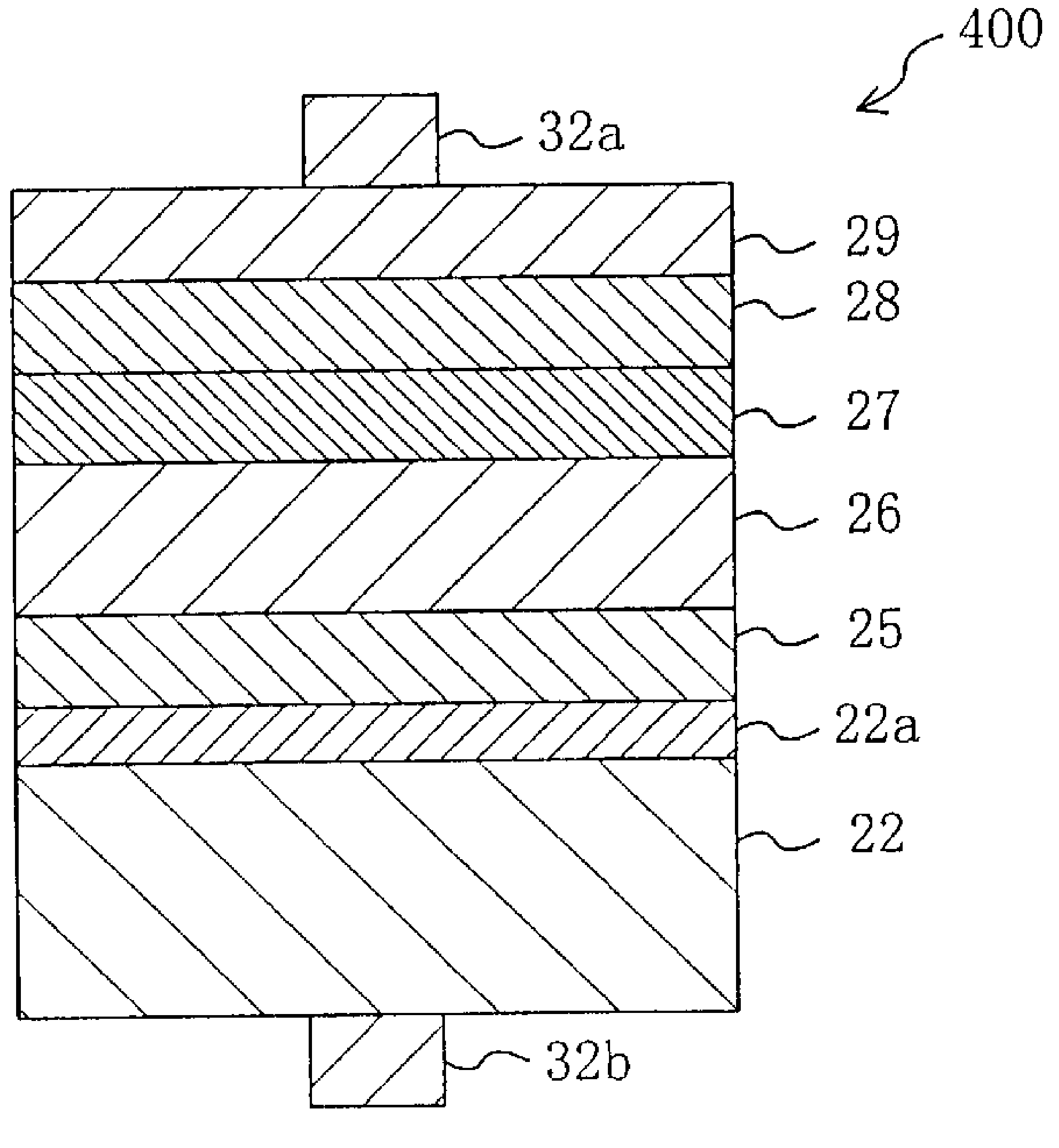


FIG. 1A

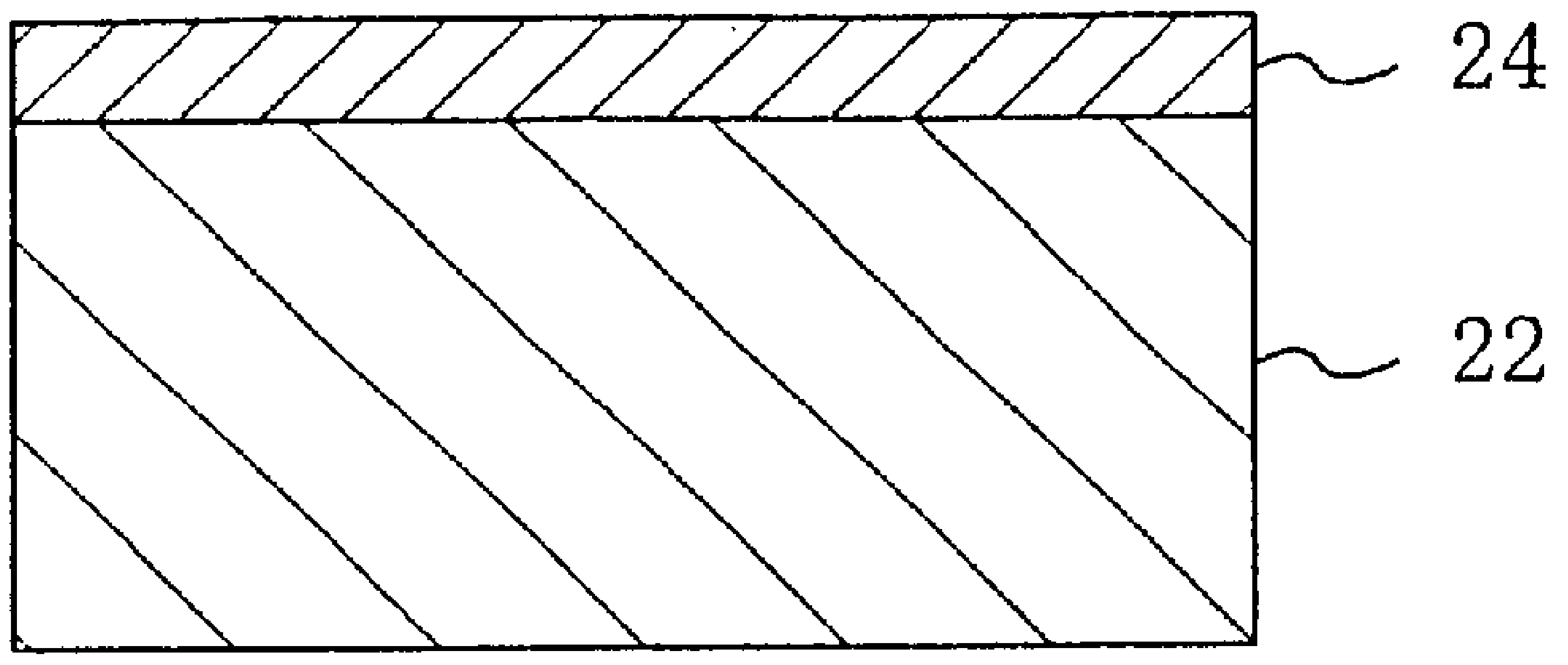


FIG. 1B

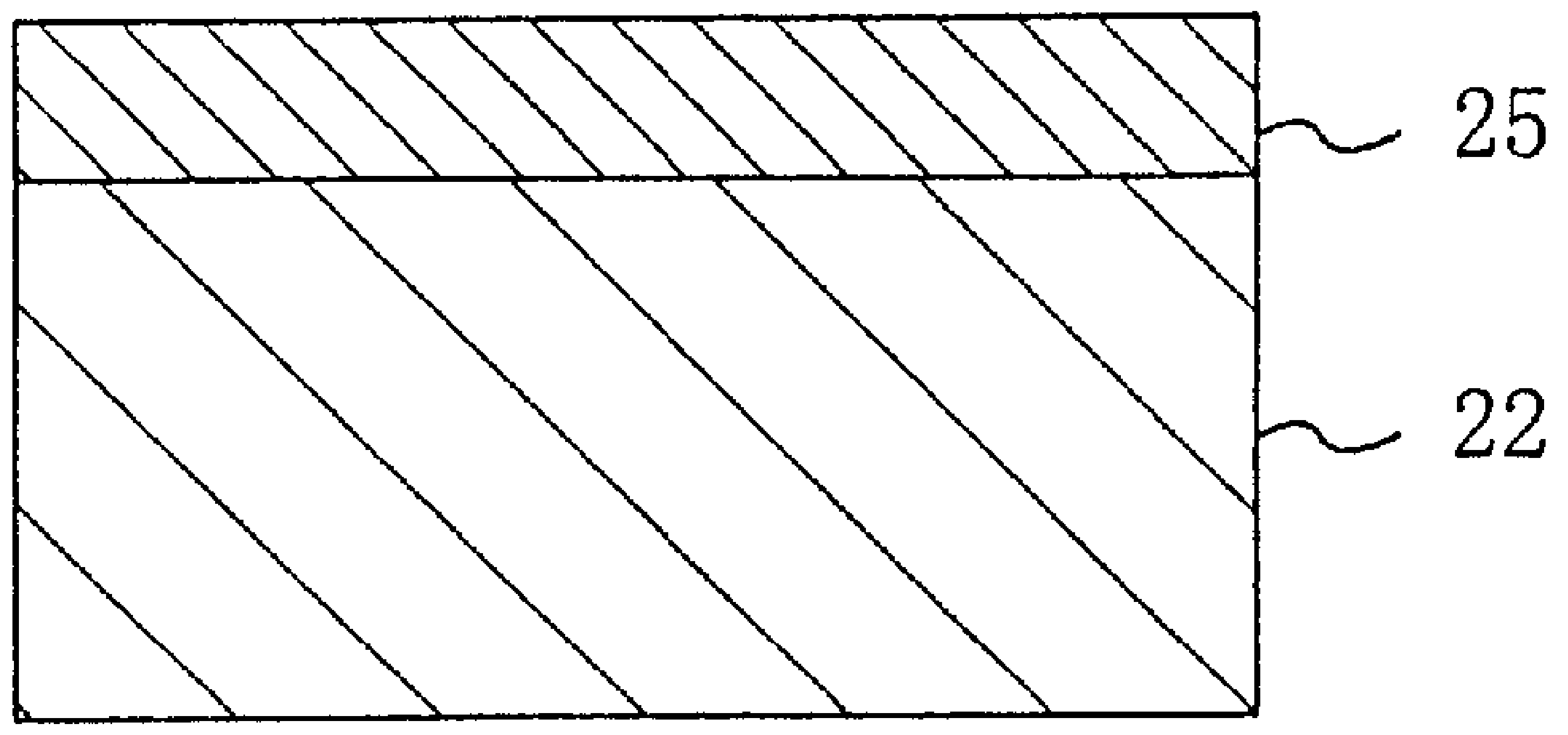


FIG. 1C

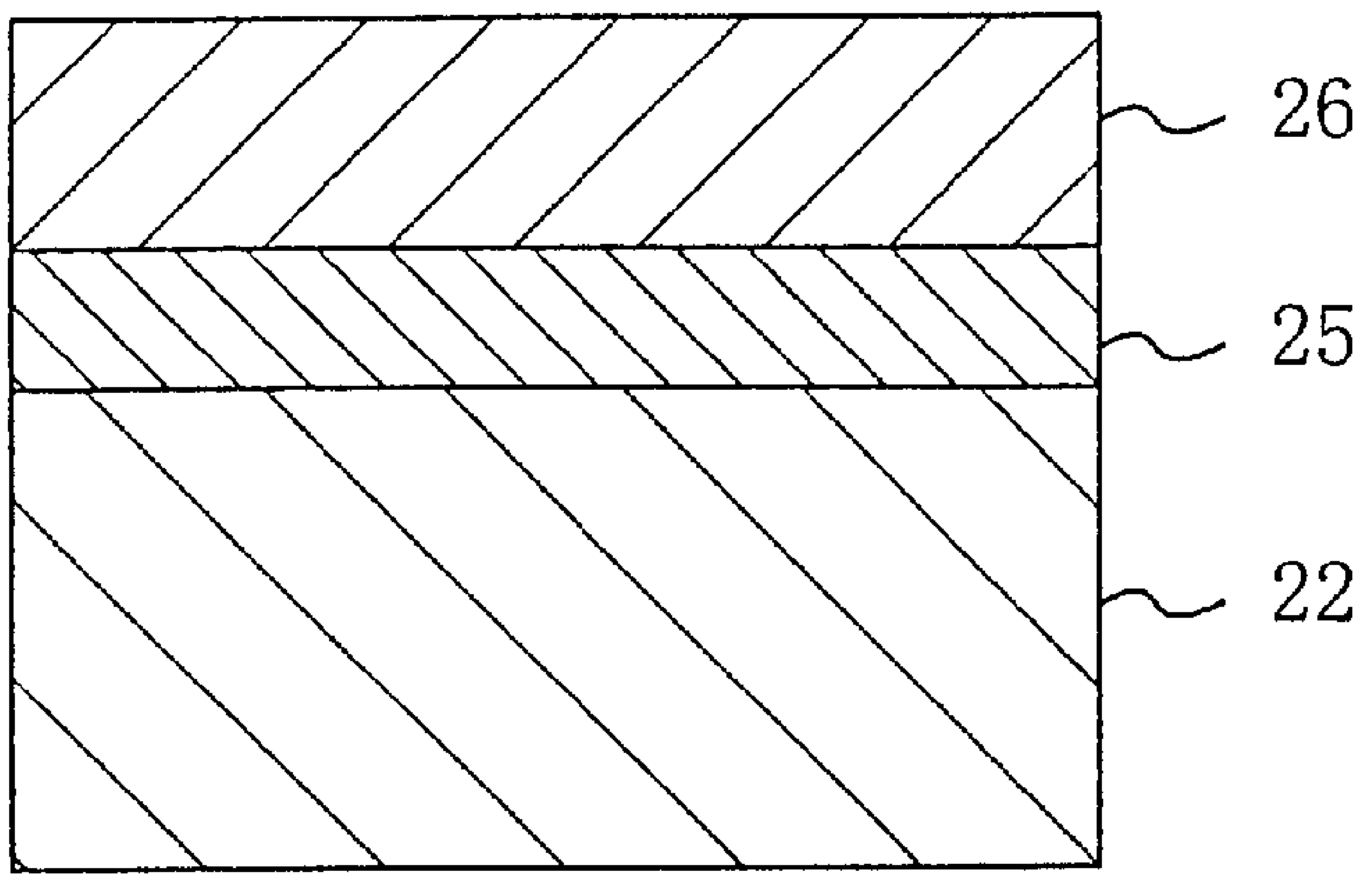


FIG. 2A

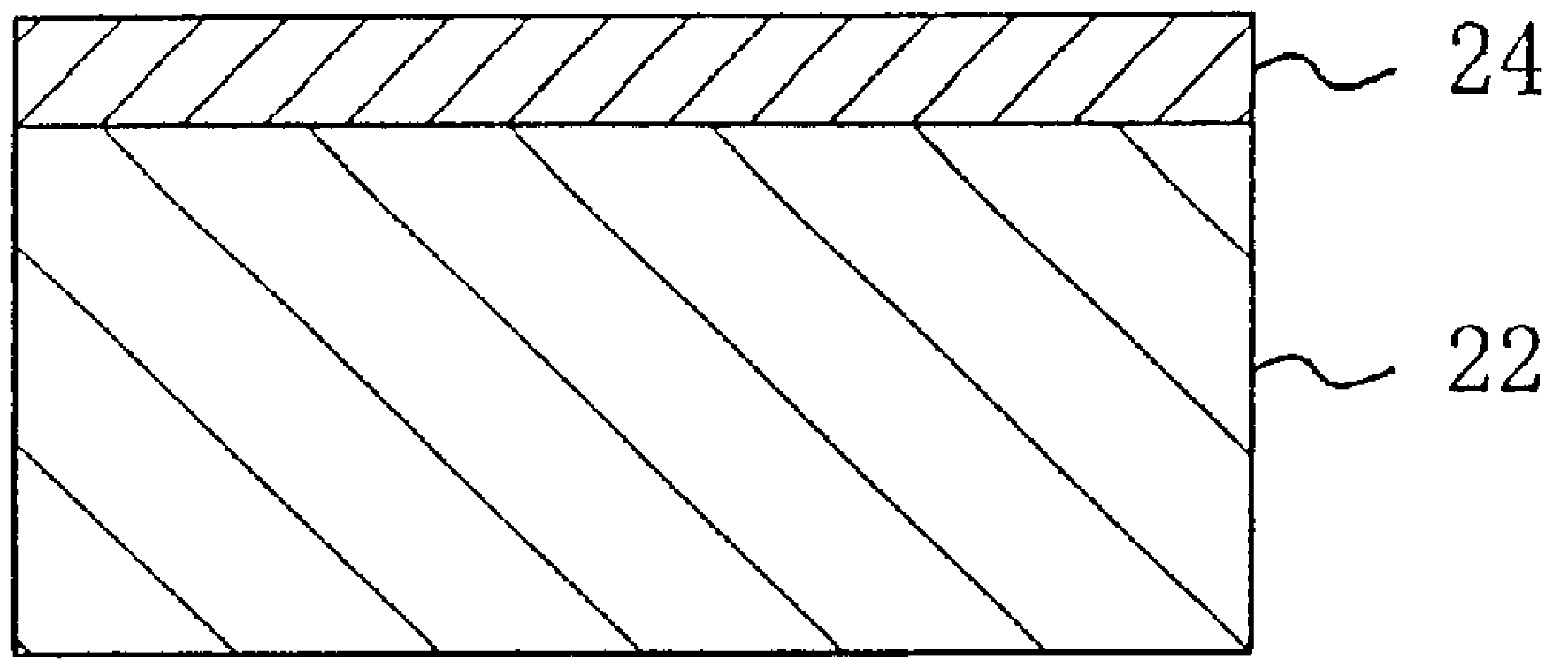


FIG. 2B

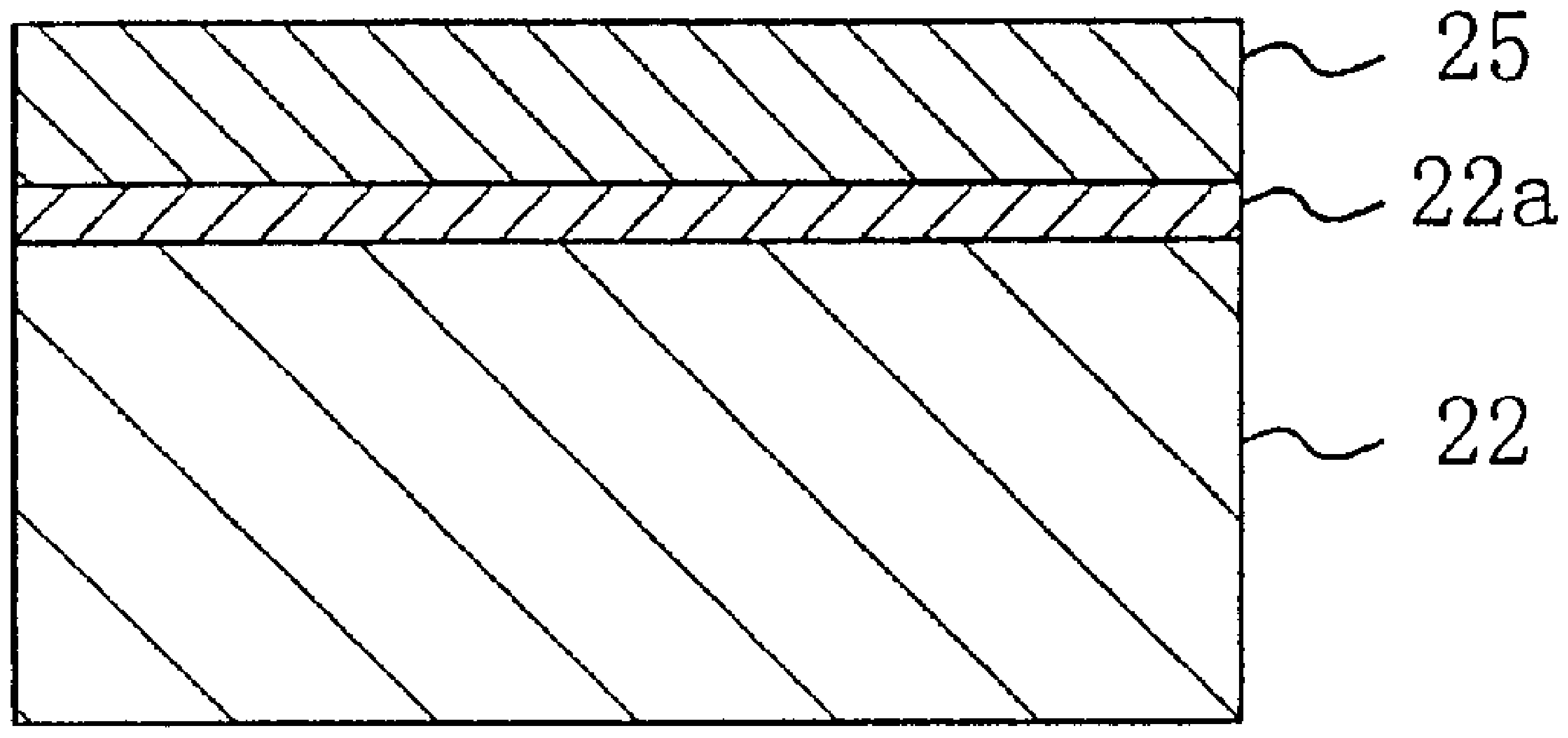


FIG. 2C

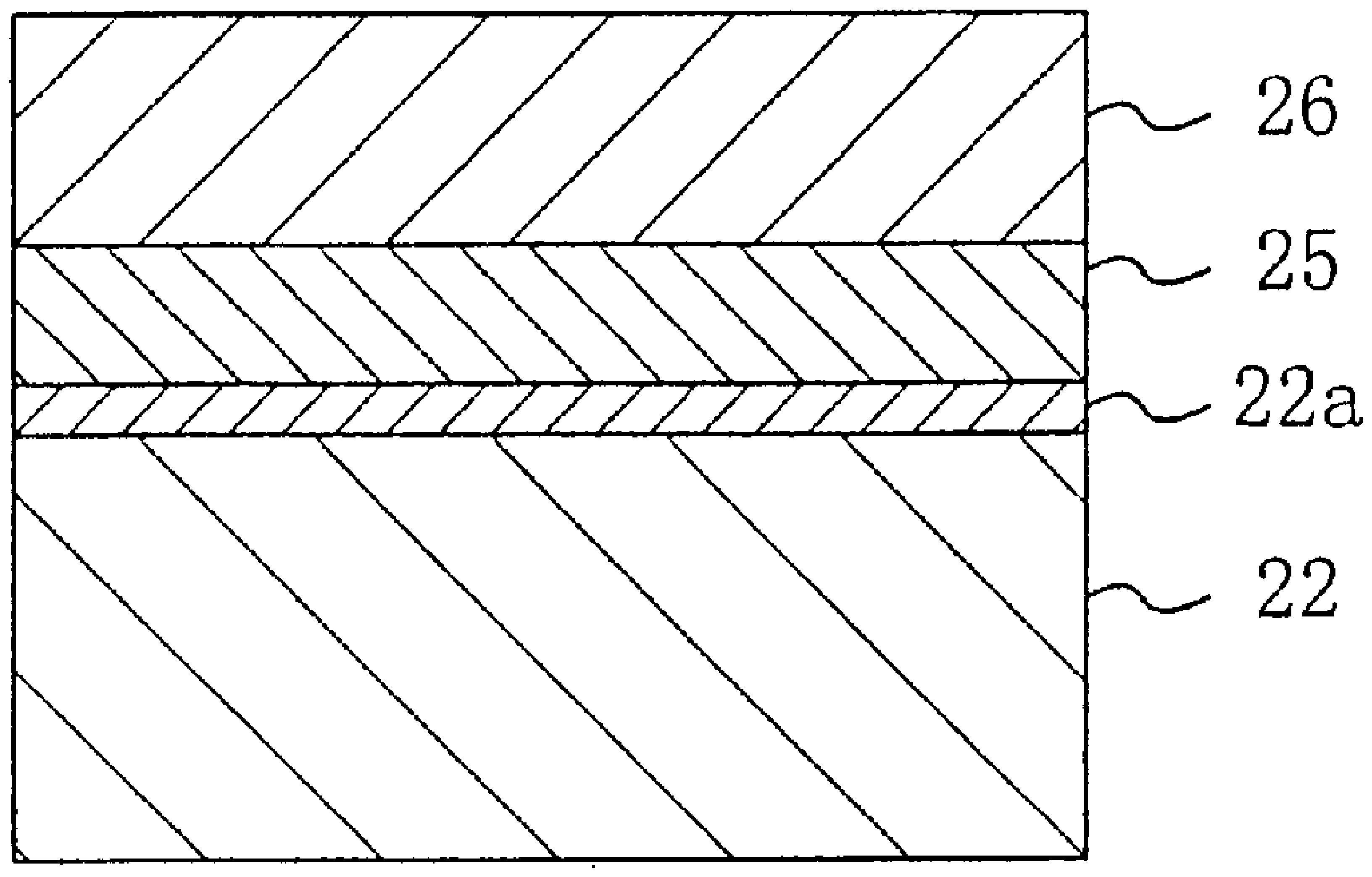


FIG. 3A

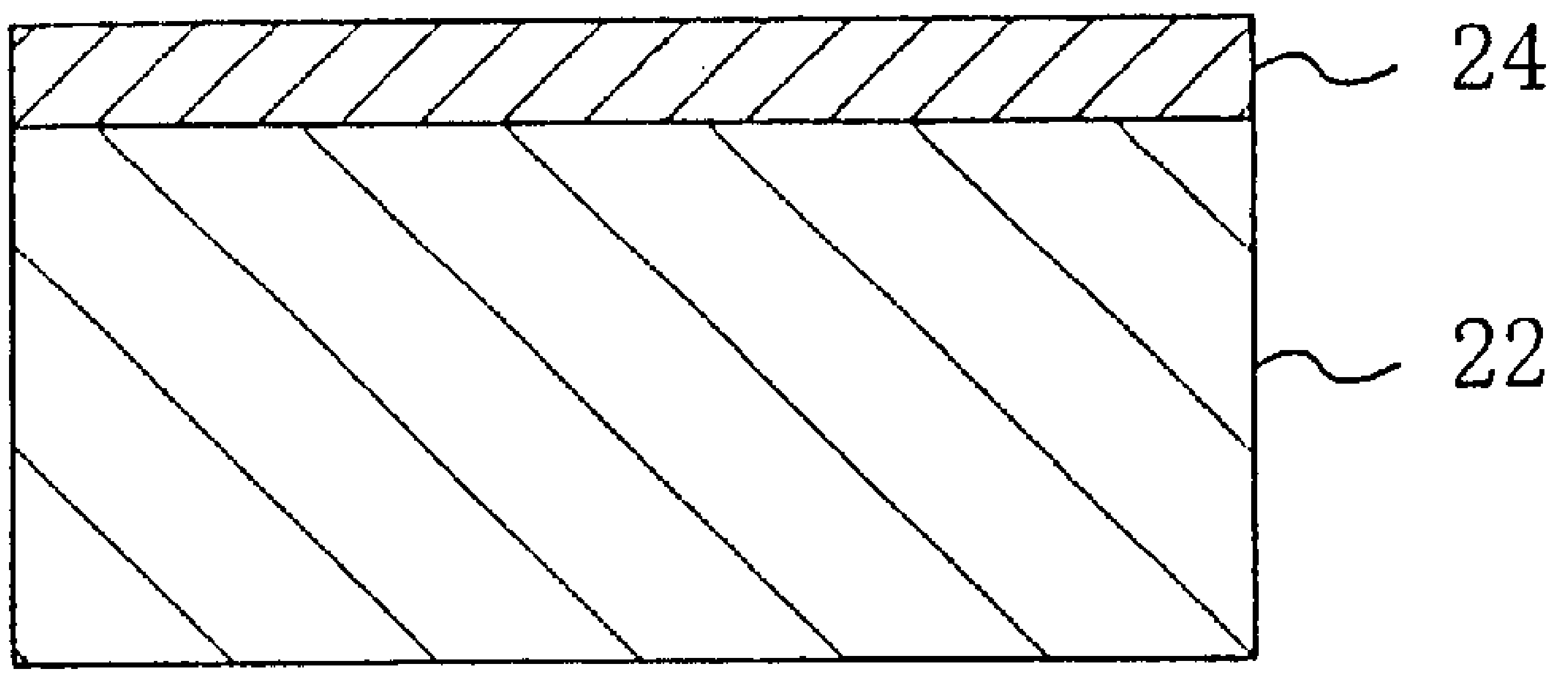


FIG. 3B

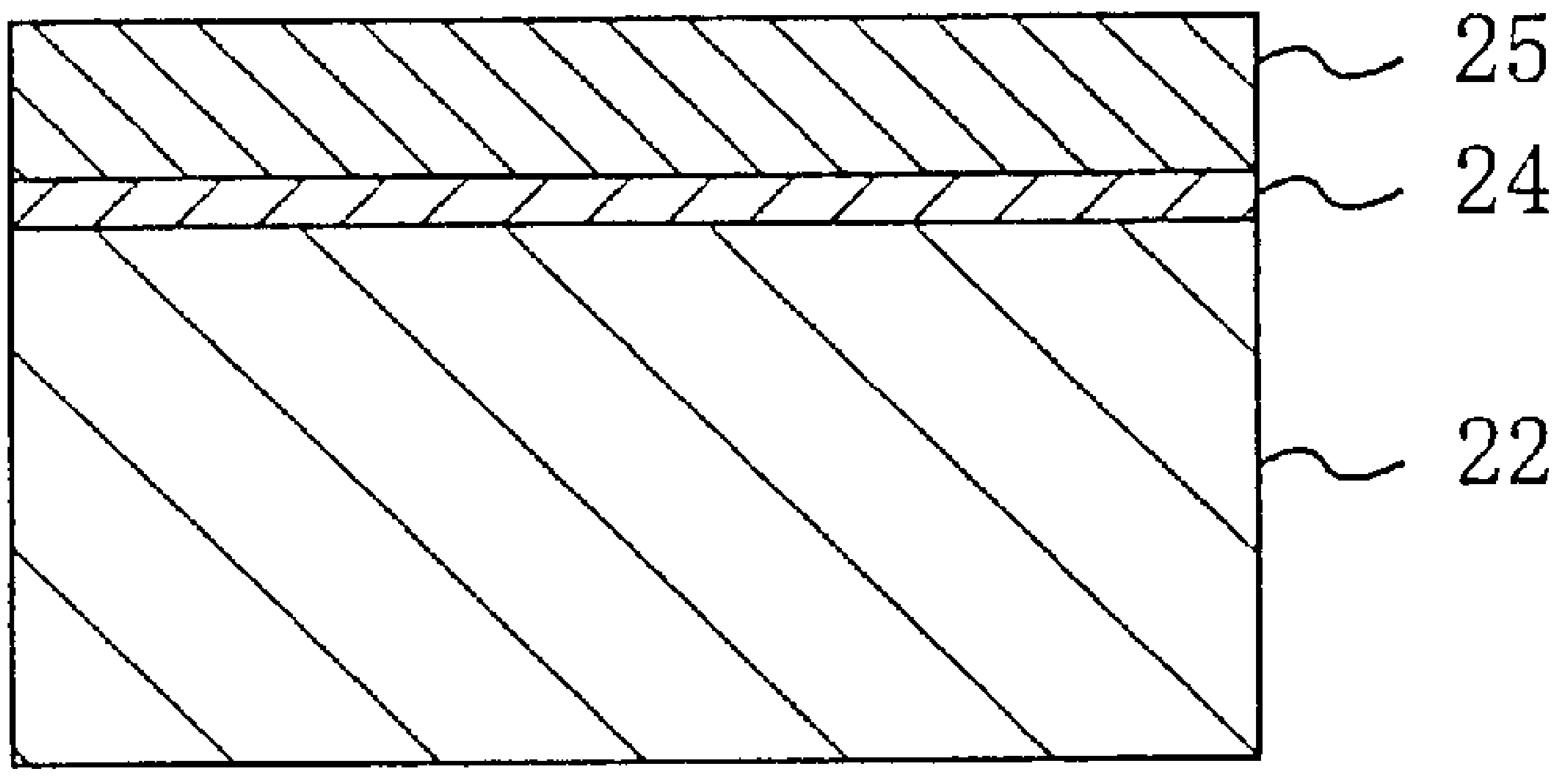


FIG. 3C

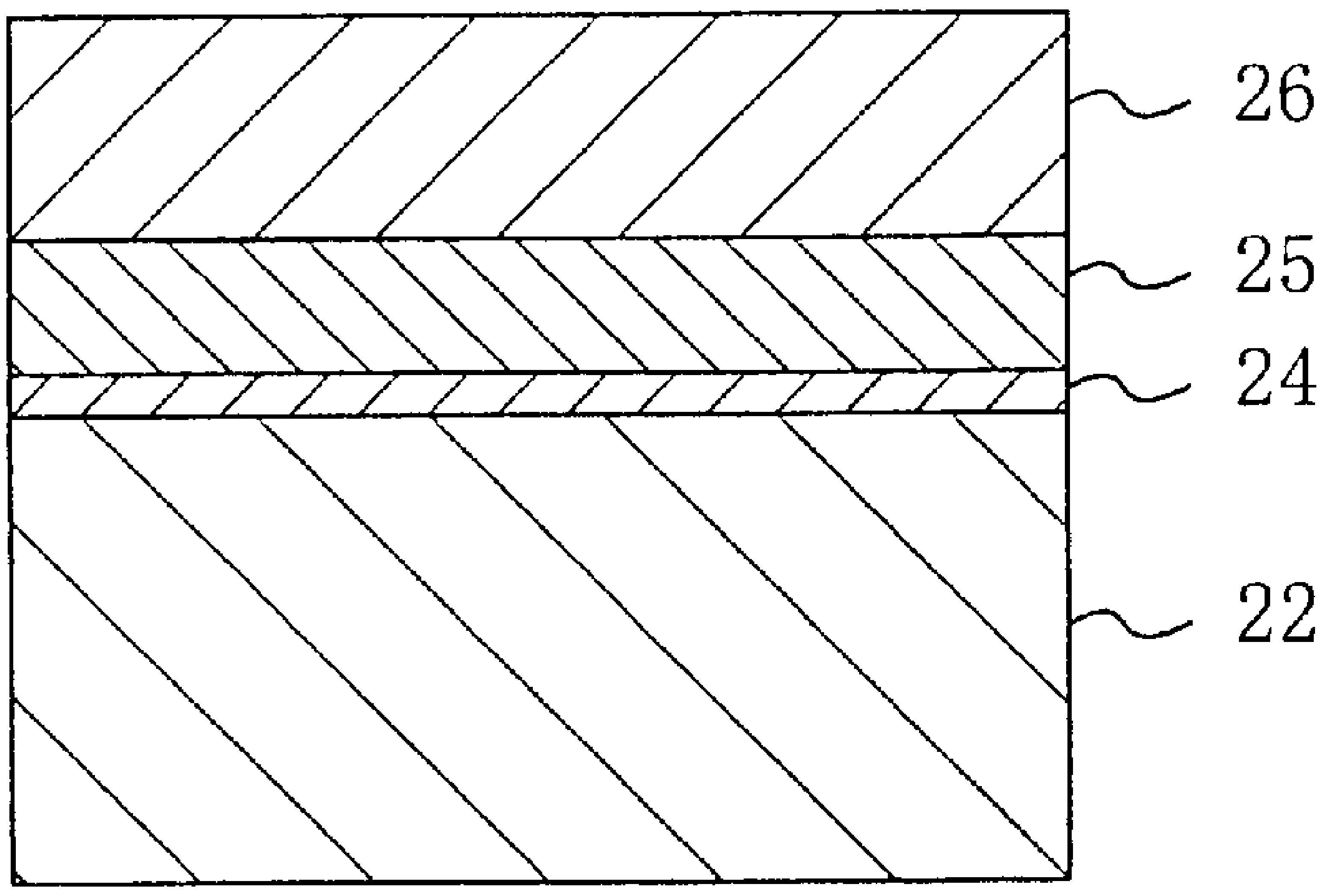


FIG. 4A

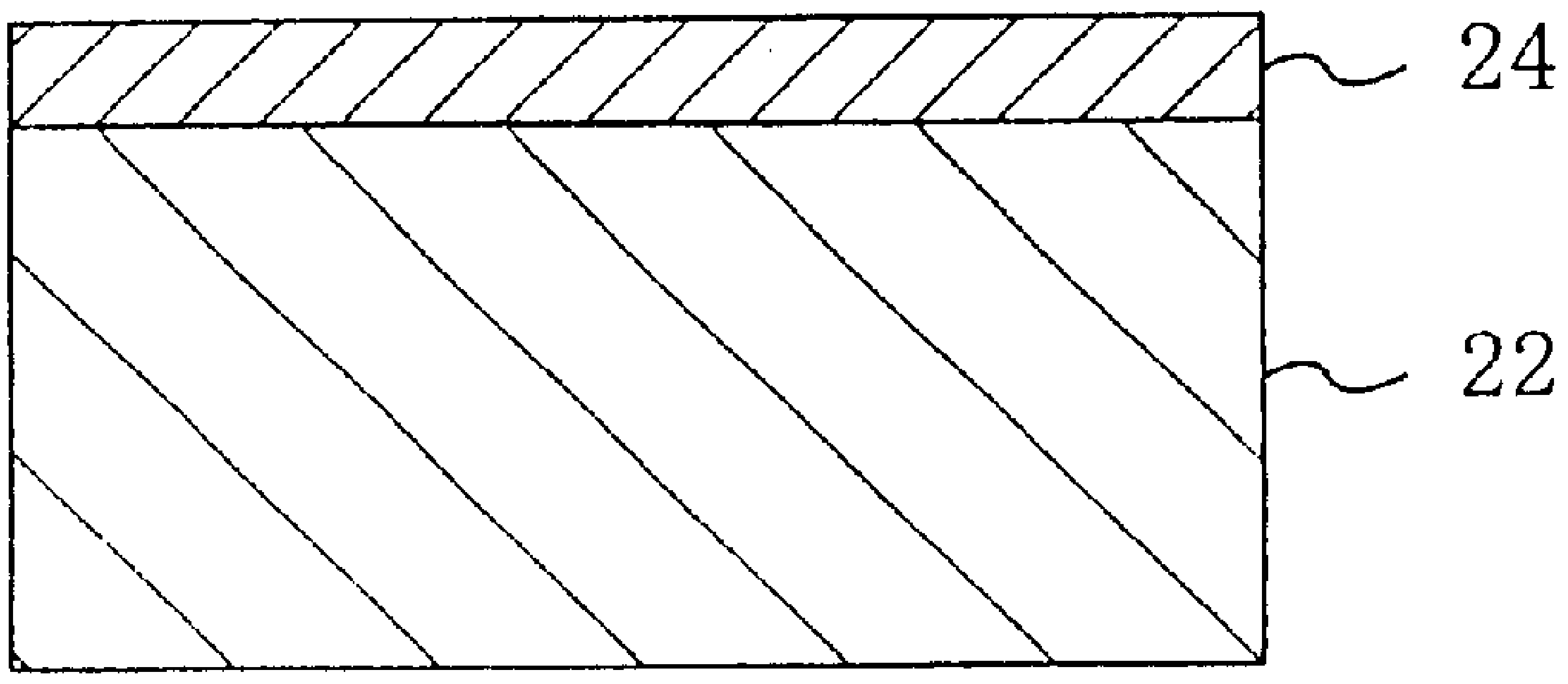


FIG. 4B

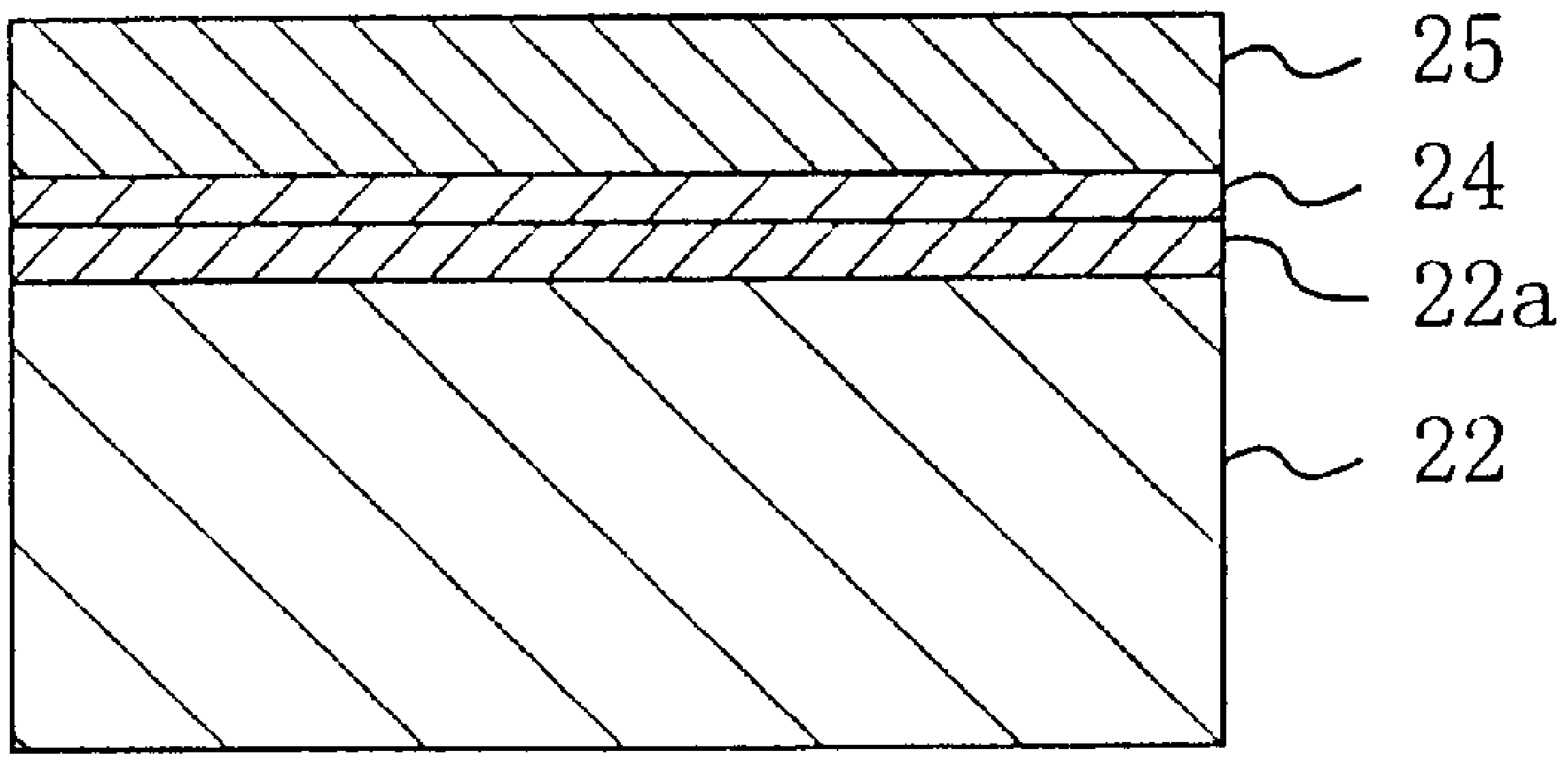


FIG. 4C

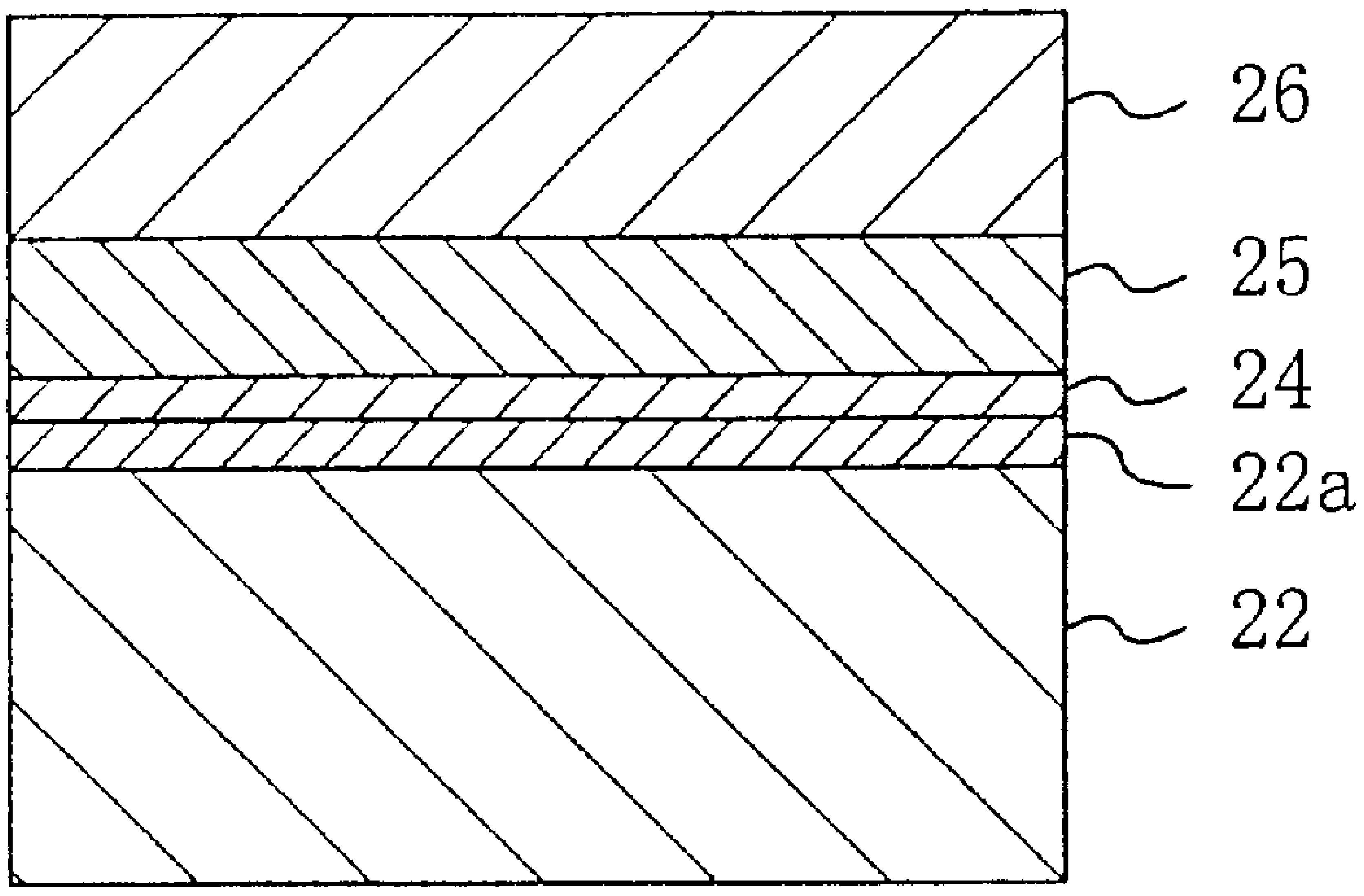


FIG. 5A

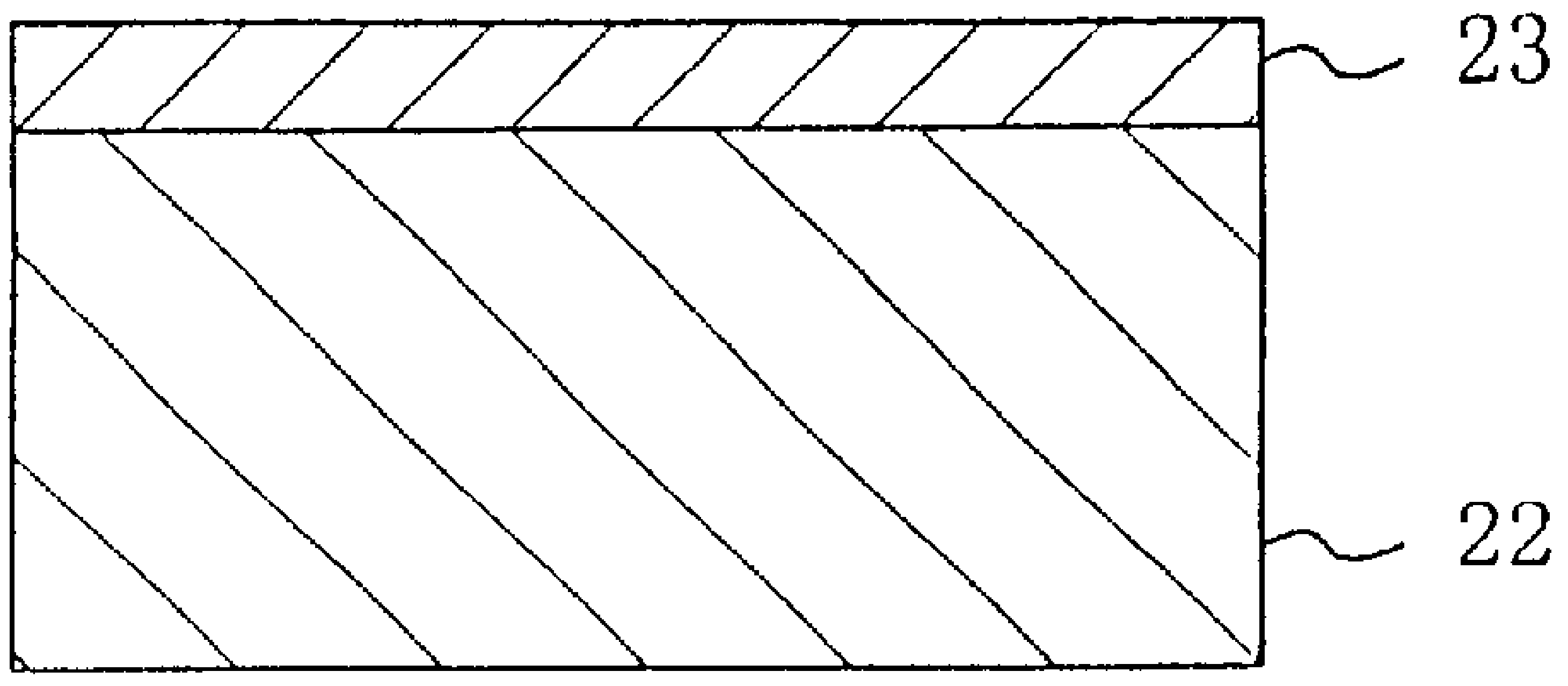


FIG. 5B

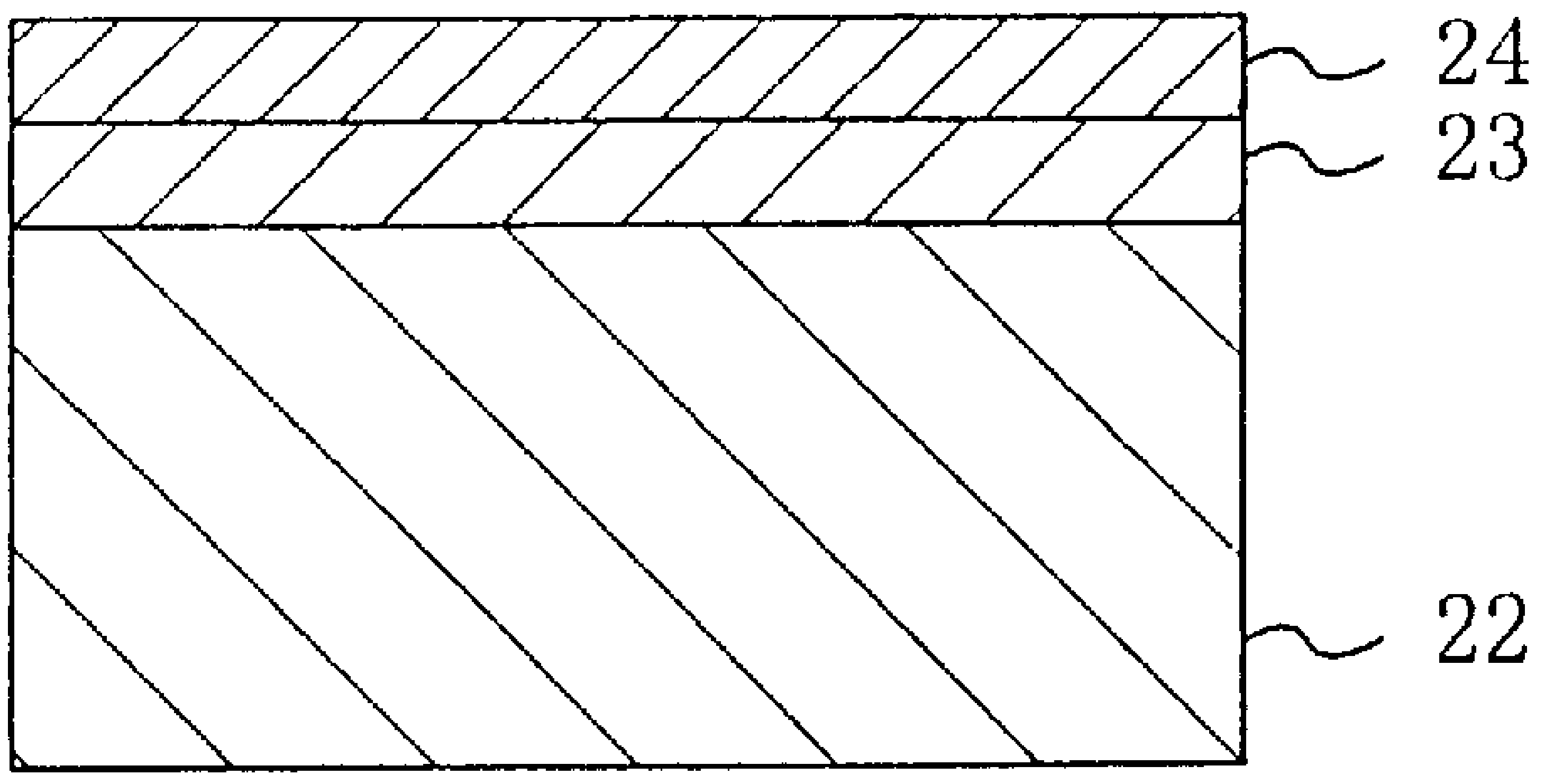


FIG. 5C

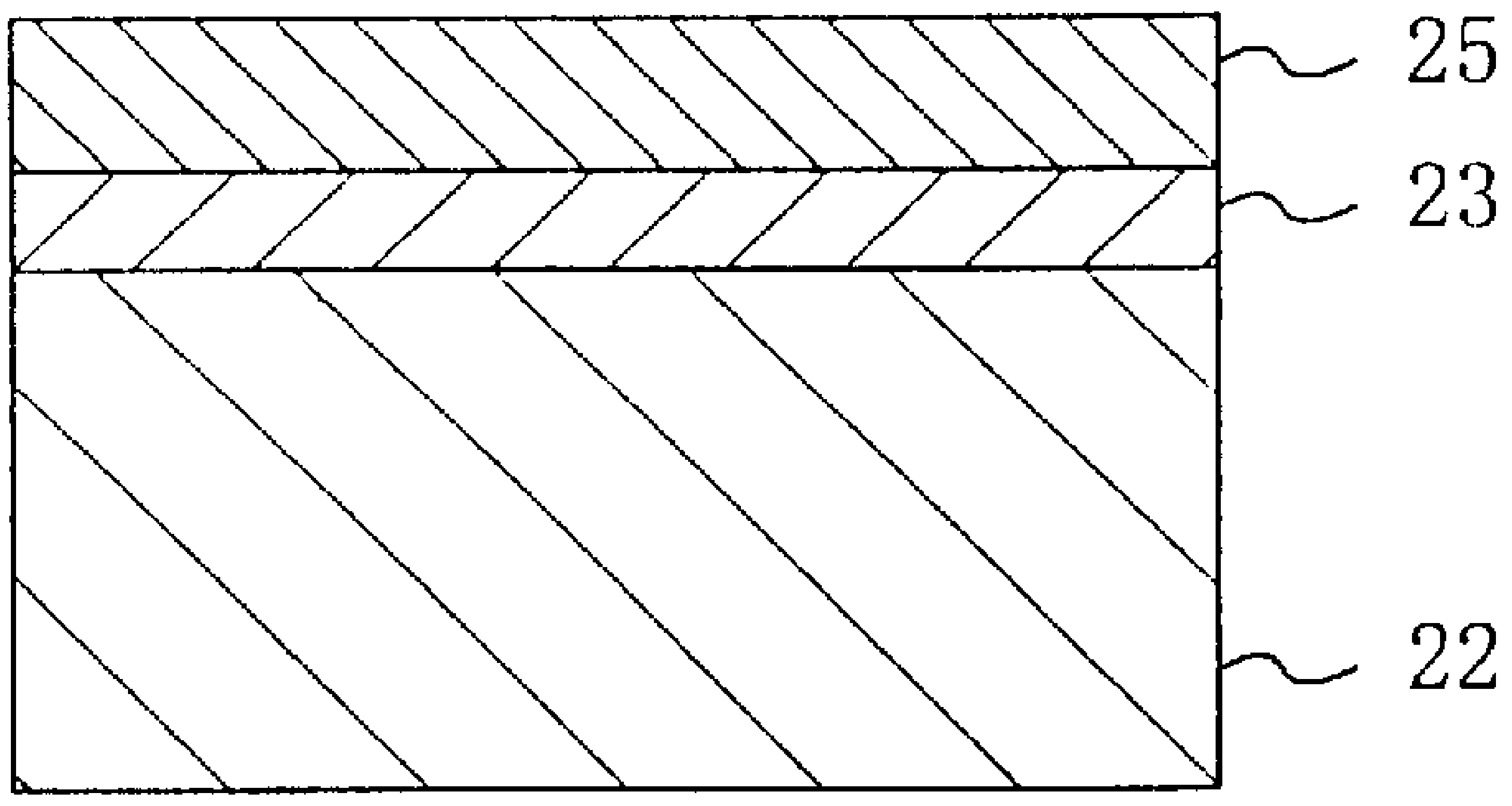


FIG. 5D

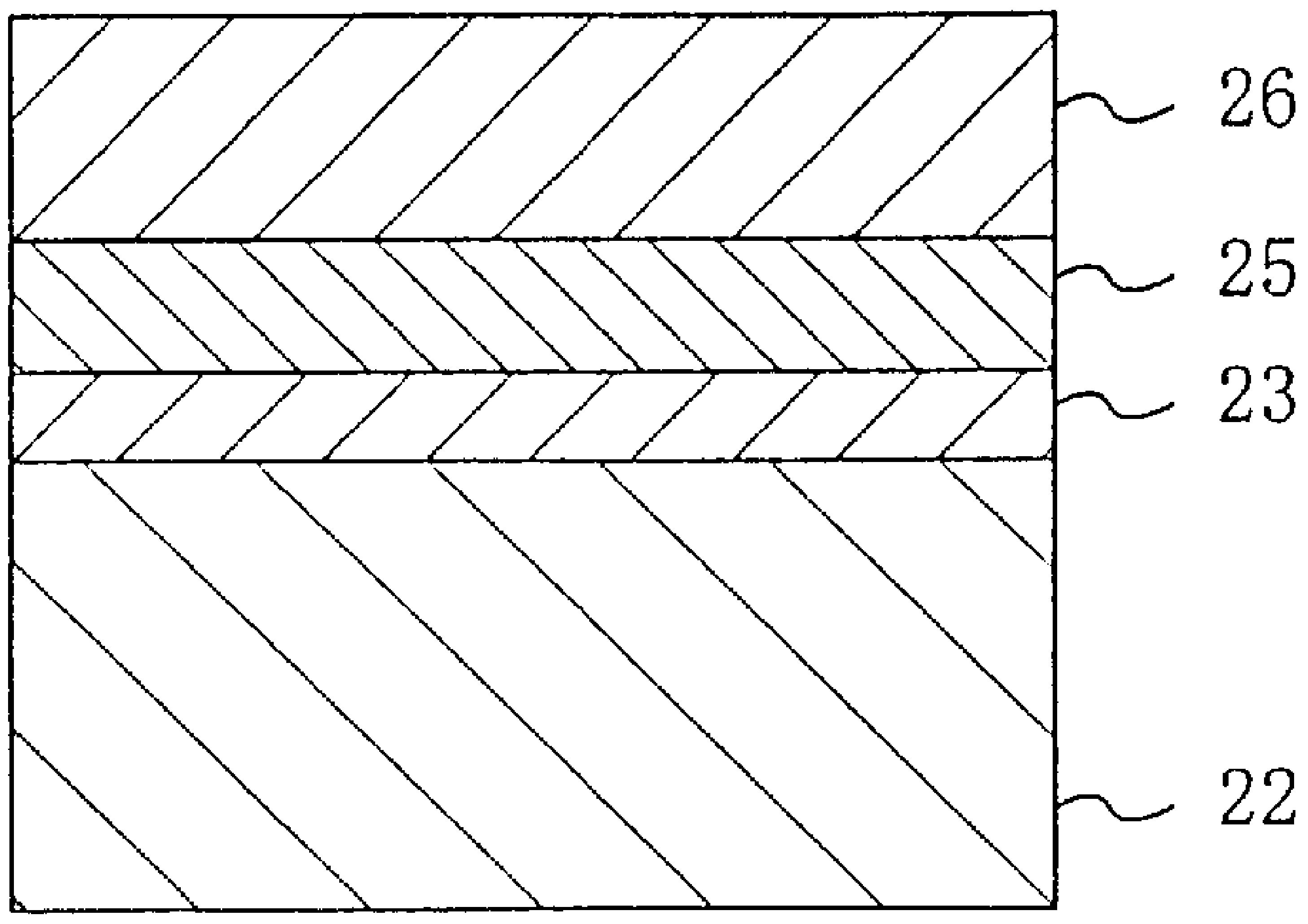


FIG. 6A

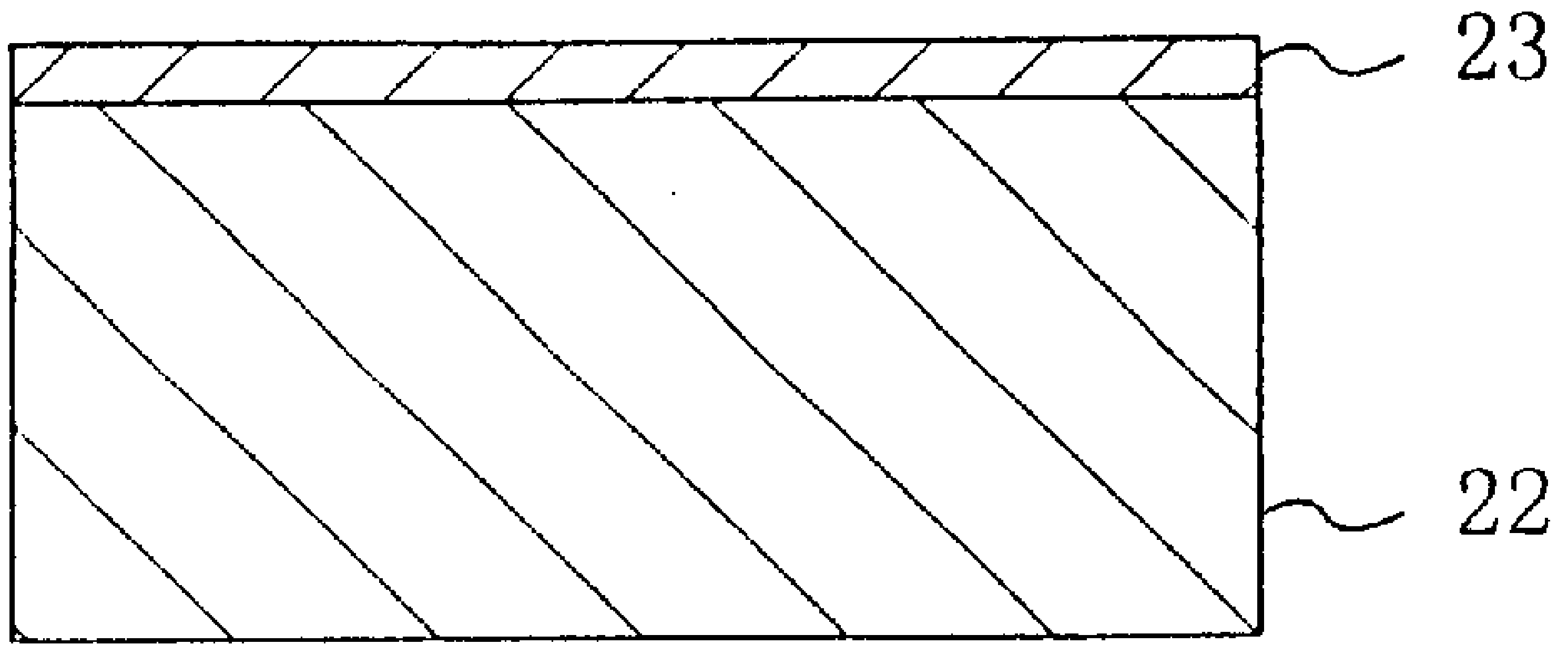


FIG. 6B

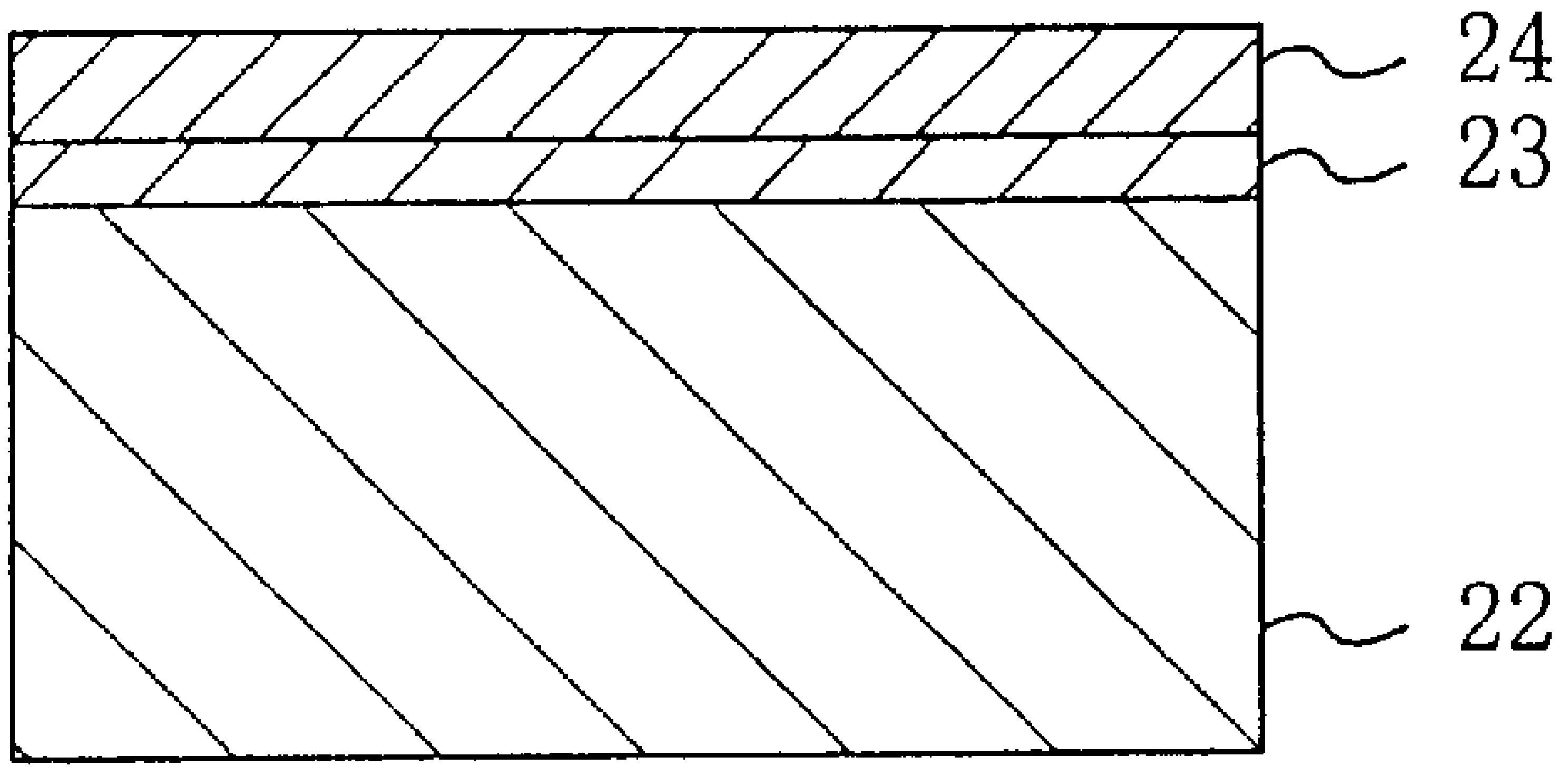


FIG. 6C

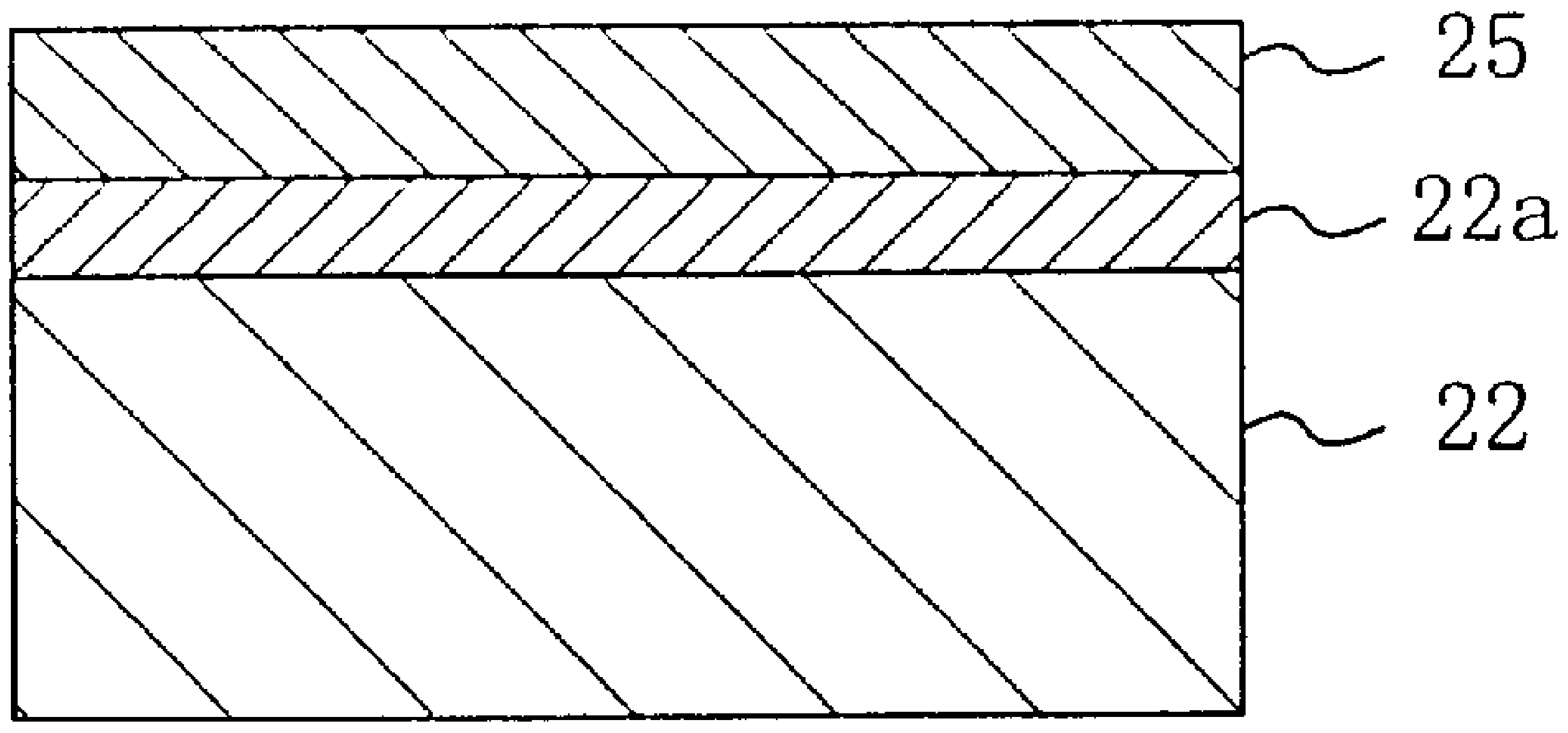


FIG. 6D

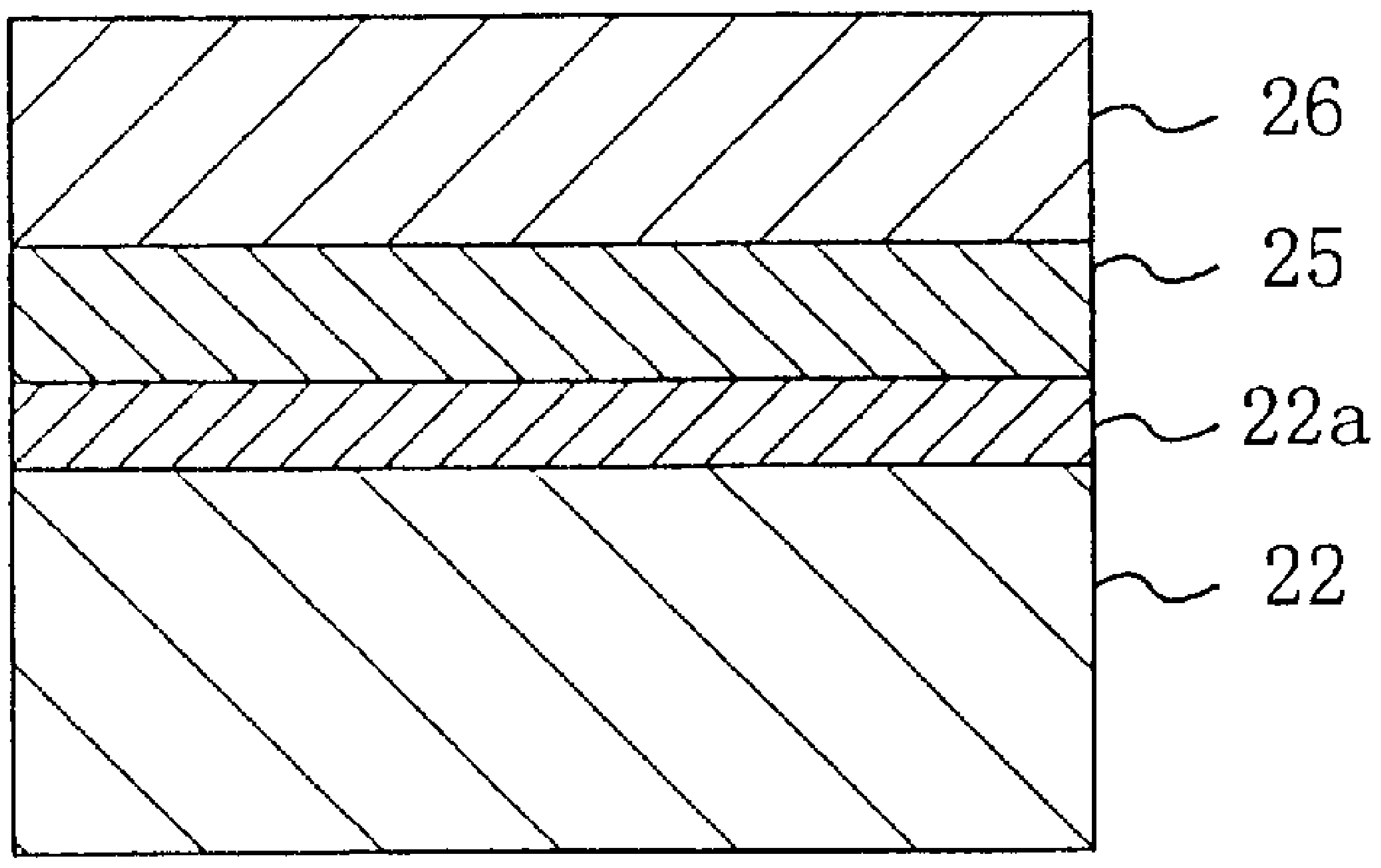


FIG. 7

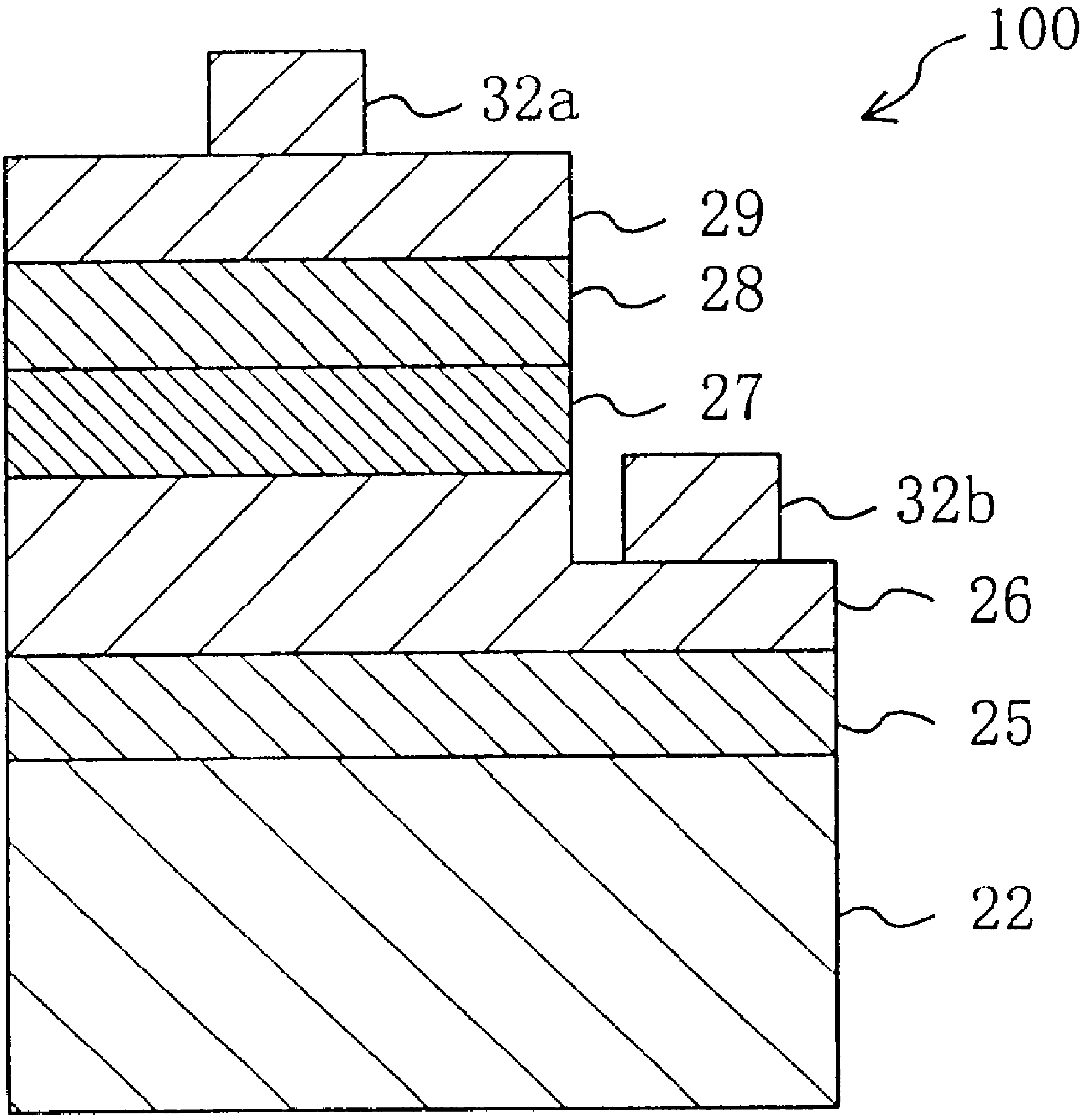


FIG. 8A

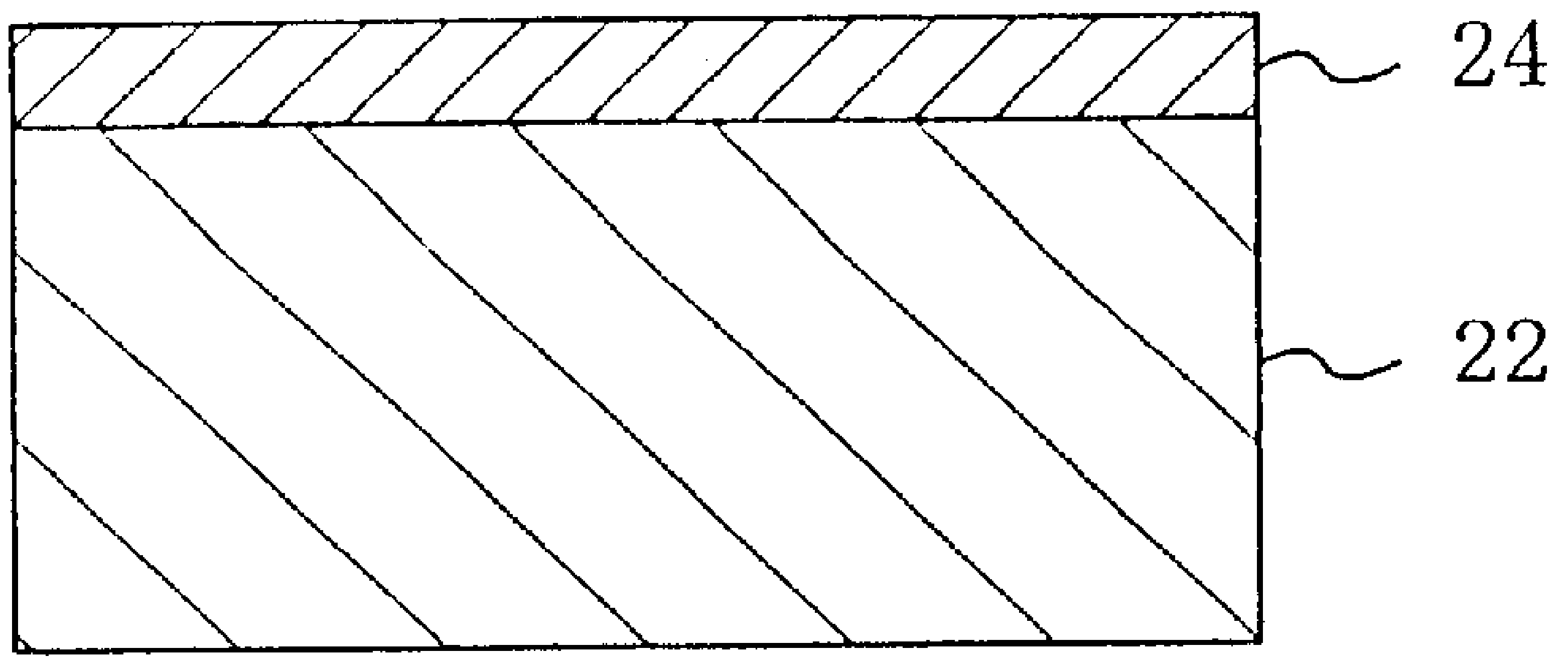


FIG. 8B

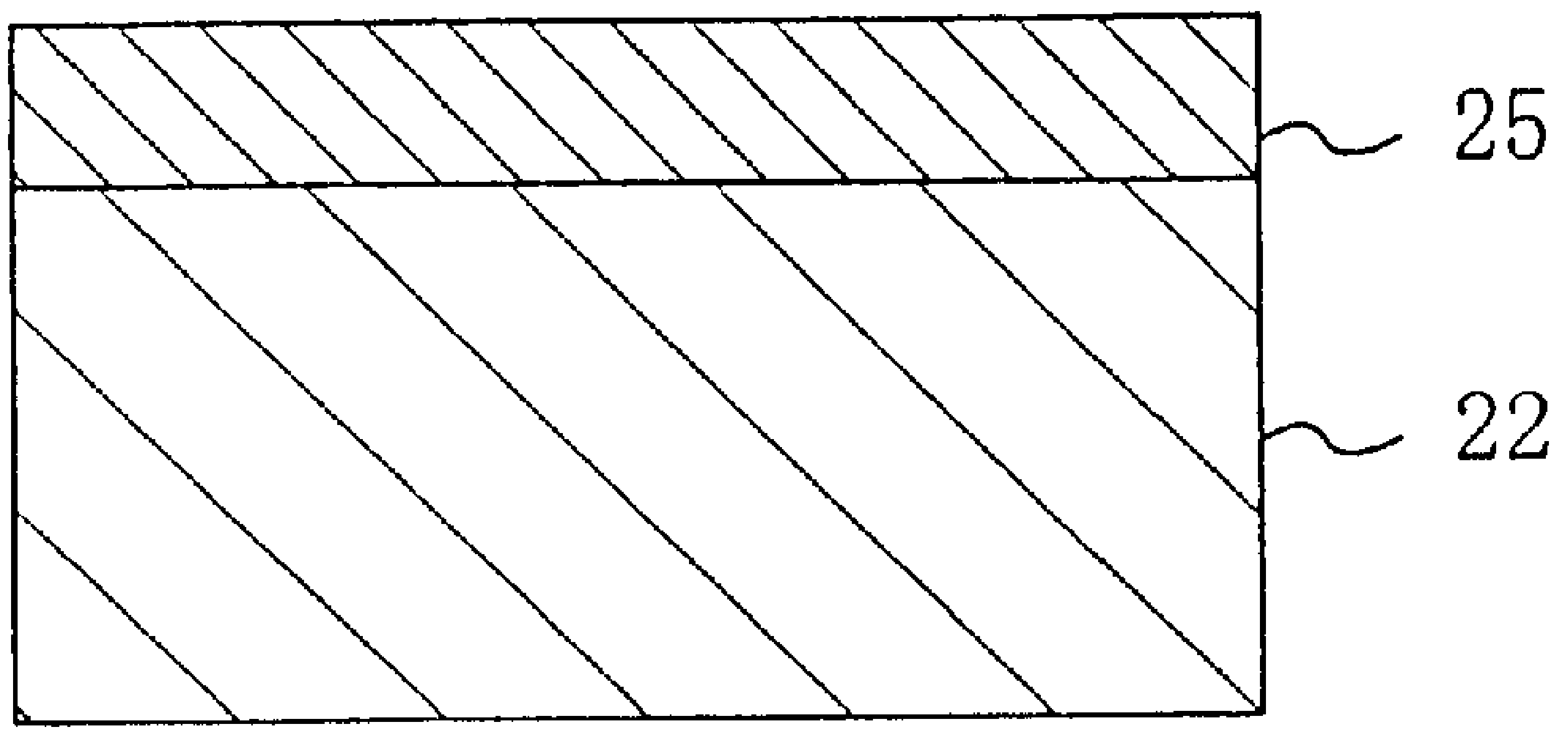


FIG. 8C

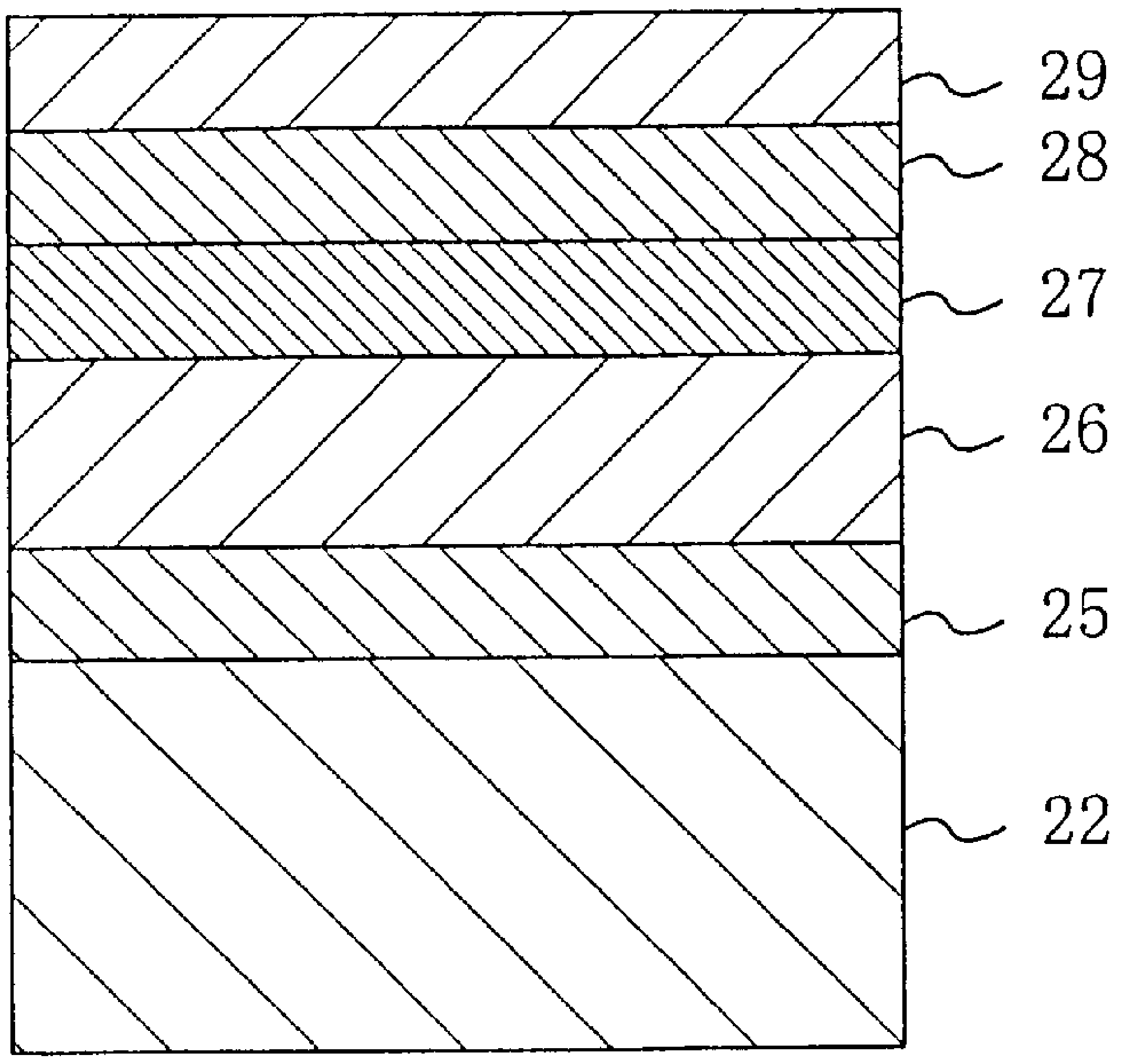


FIG. 9

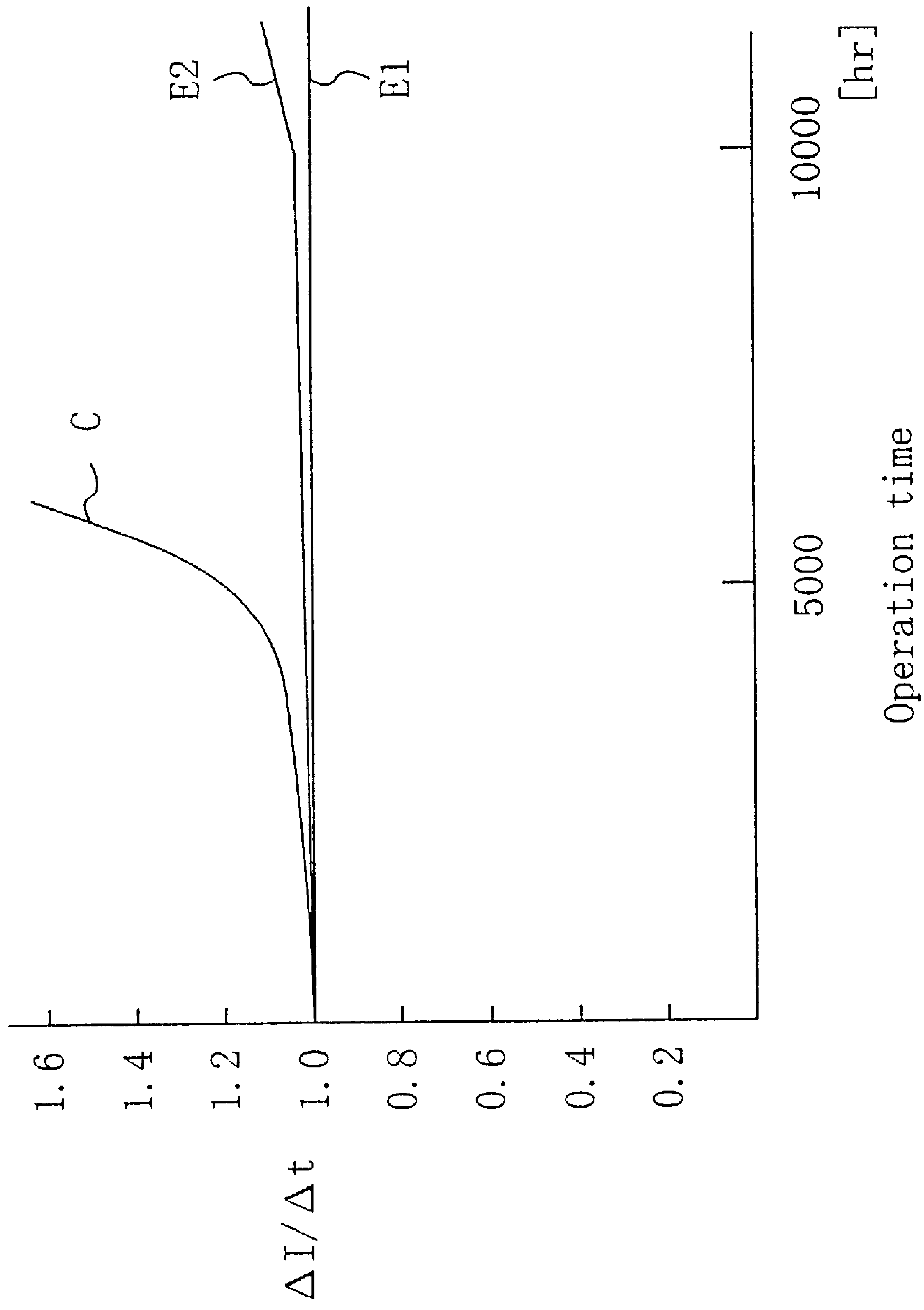


FIG. 10

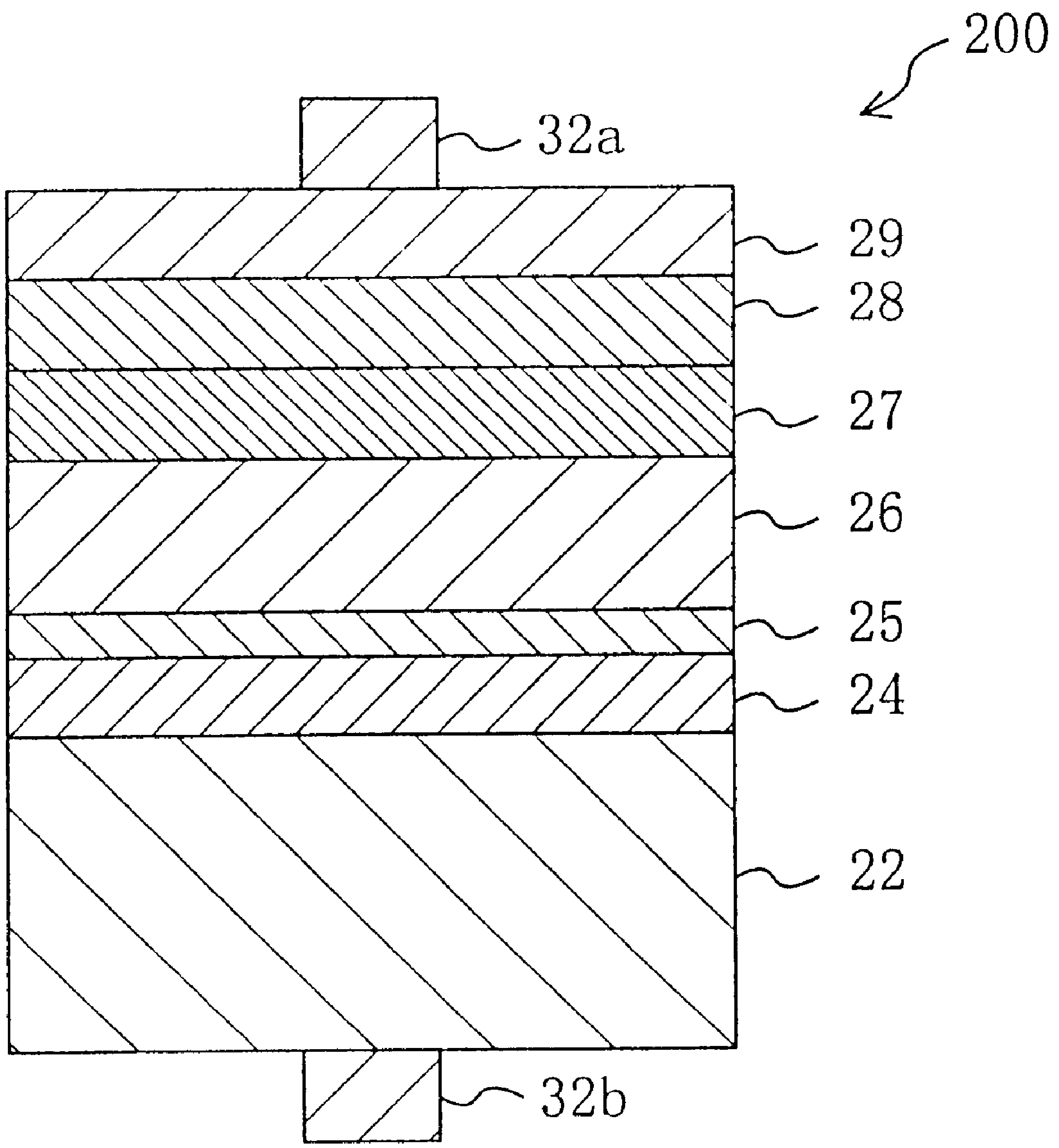


FIG. 11A

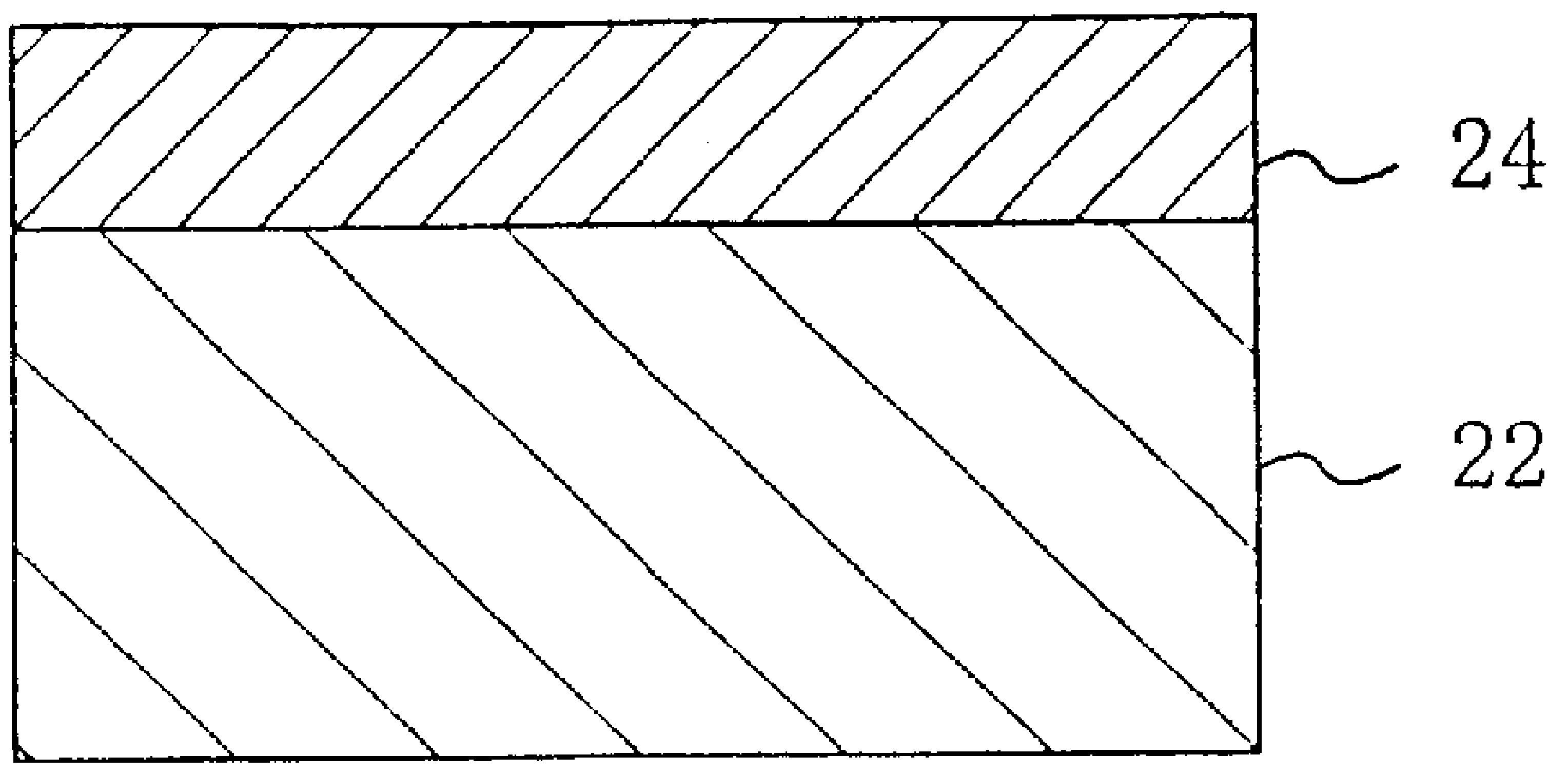


FIG. 11B

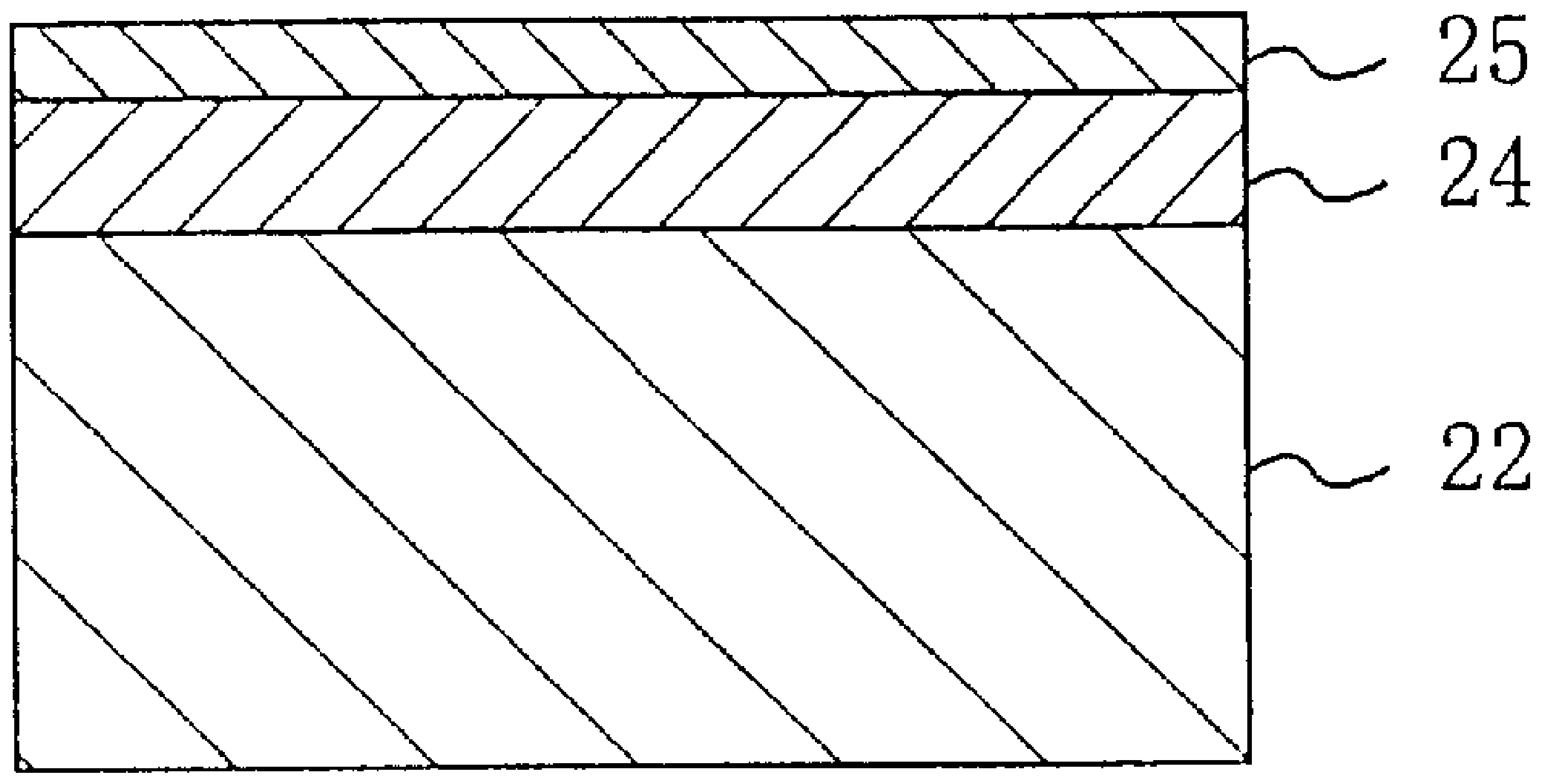


FIG. 11C

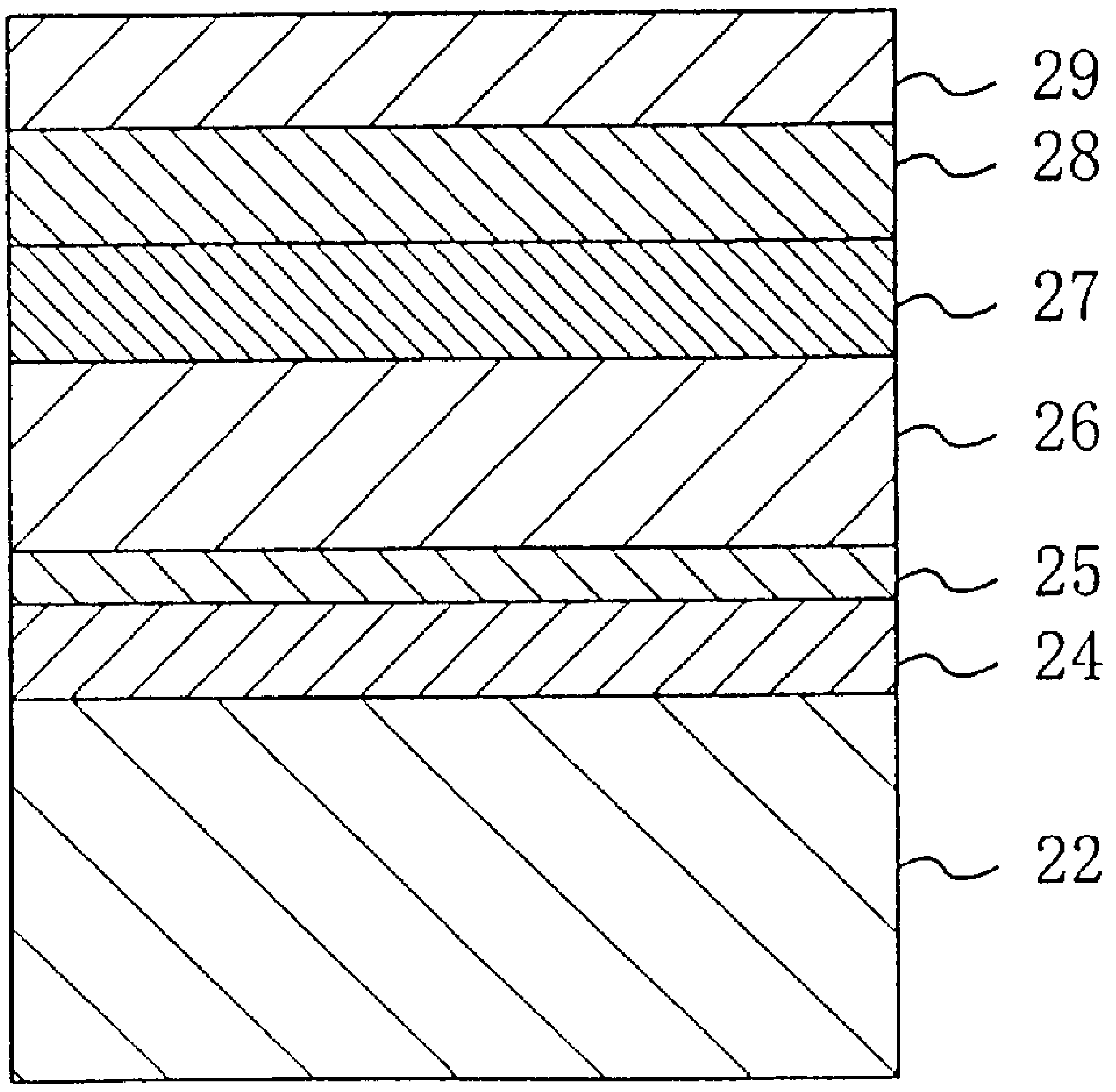


FIG. 12

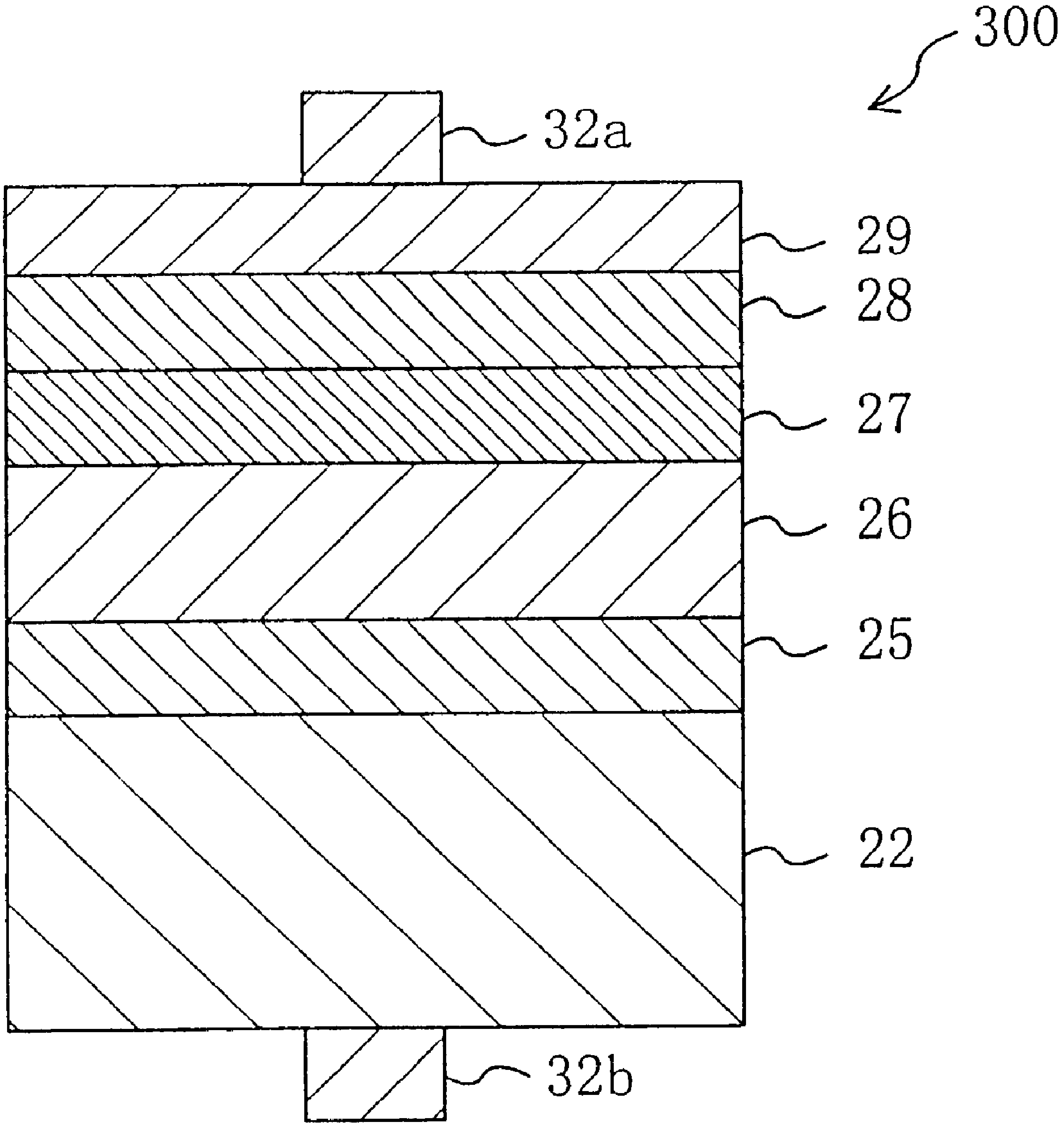


FIG. 13

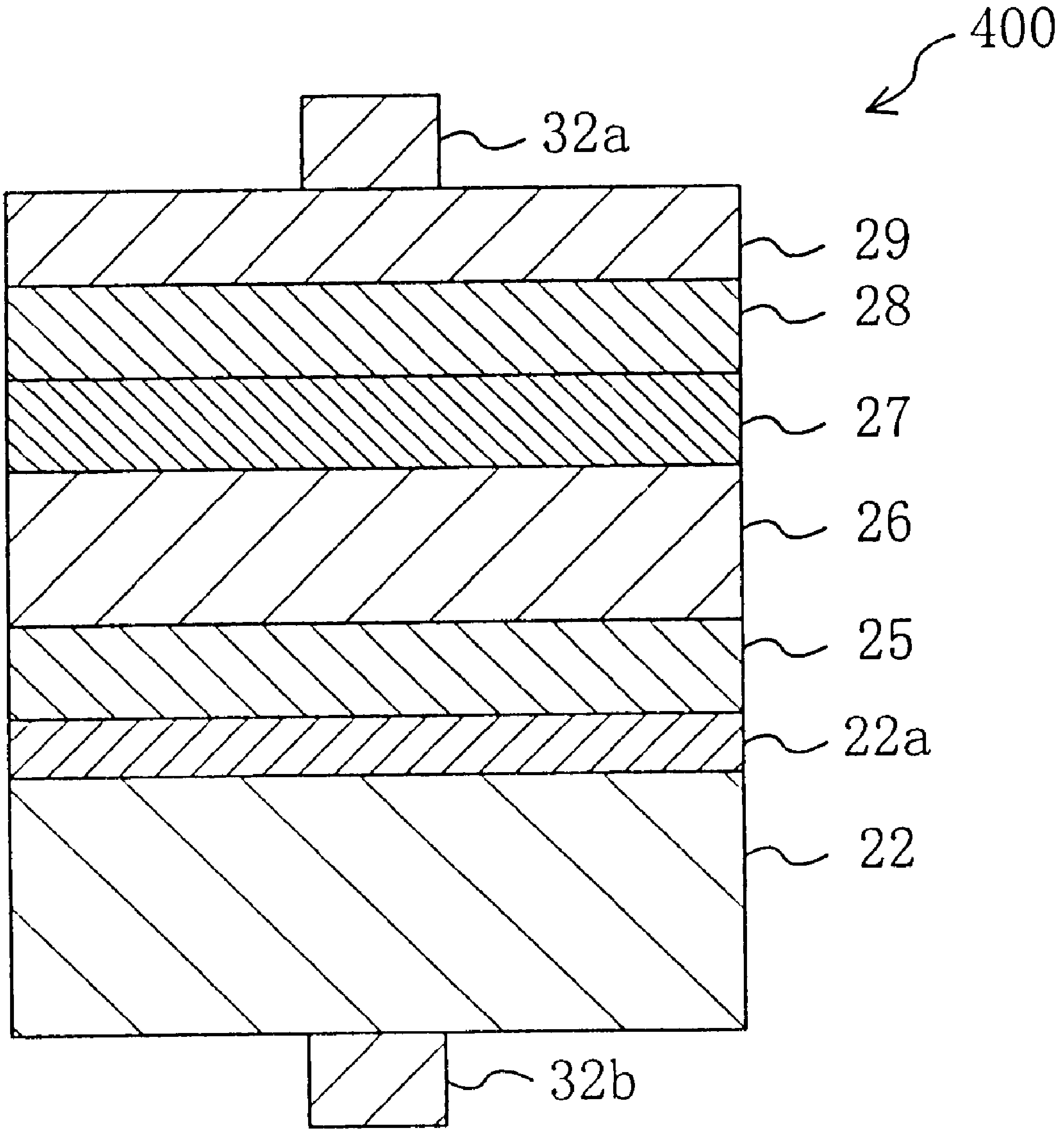
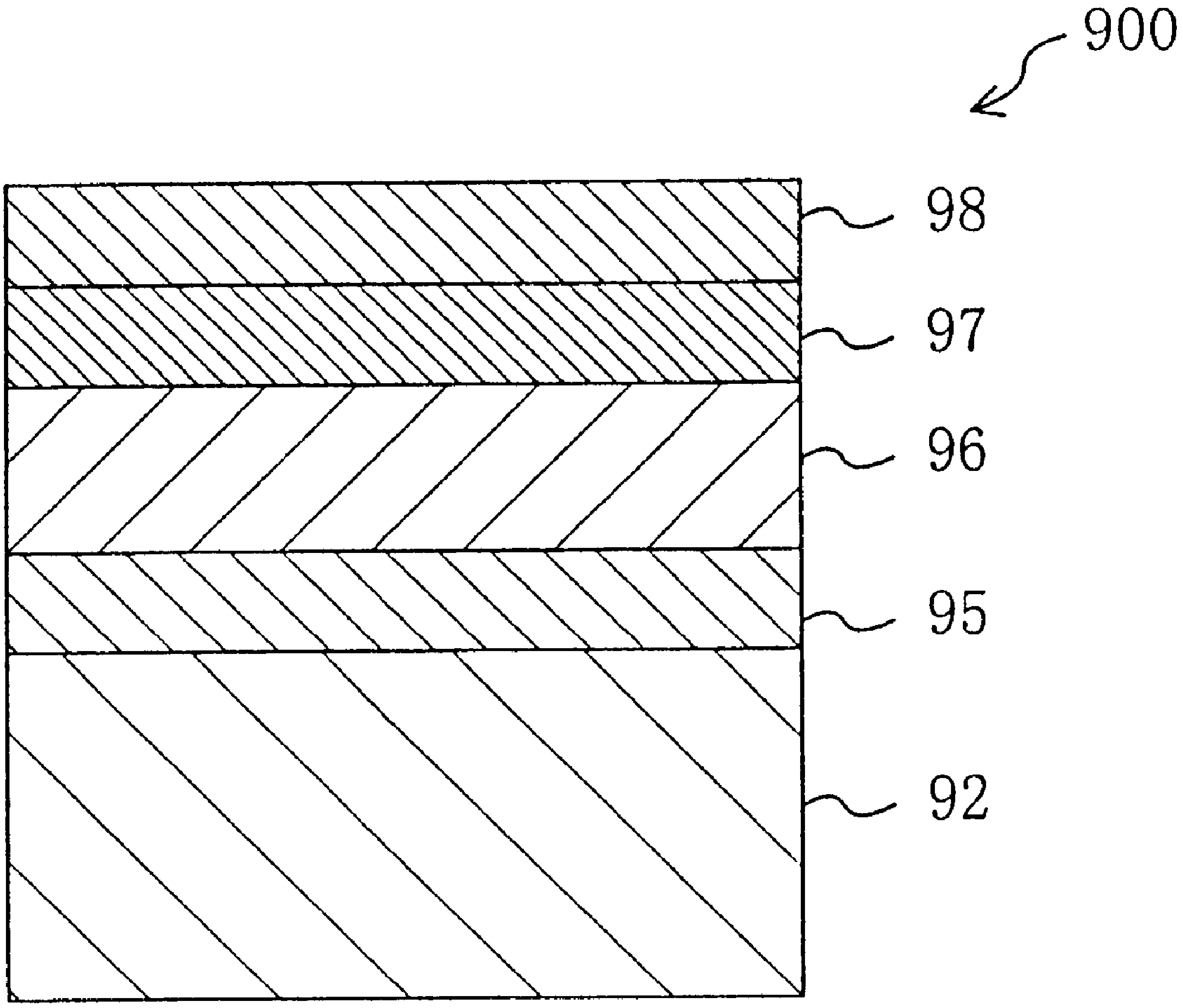


FIG. 14
PRIOR ART



METHOD FOR GROWING NITRIDE SEMICONDUCTOR CRYSTALS, NITRIDE SEMICONDUCTOR DEVICE, AND METHOD FOR FABRICATING THE SAME

BACKGROUND OF THE INVENTION

The present invention relates to a method for growing nitride semiconductor crystals, a nitride semiconductor device and a method for fabricating the same.

Nitride semiconductors such as GaN, InN and AlN are materials suitably used for blue-light-emitting semiconductor laser devices and numerous types of semiconductor devices, e.g., transistors operating at a high speed at an elevated temperature.

Various methods have been suggested to form a single crystal layer of a nitride semiconductor suitable for these semiconductor devices.

For example, according to a conventional technique, a nitride semiconductor layer (e.g., an AlN layer) is directly deposited on a single crystal substrate of sapphire (Al_2O_3) or Si by a metalorganic vapor phase epitaxy (abbreviated to "MOVPE" and also called a "metalorganic chemical vapor deposition (MOCVD)") process. The nitride semiconductor layer formed by this method, however, has poor surface morphology and is likely to crack, resulting in a lower yield. Thus, this method has not been put into practice. Cracking is probably caused due to a thermal stress resulting from a difference in thermal expansion coefficient between a single crystal substrate and a nitride semiconductor layer during the process of lowering the deposition temperature of the nitride semiconductor layer (about 1000° C. for AlN) to room temperature.

Another technique of forming a single crystalline nitride semiconductor layer was developed later as disclosed in Japanese Laid-Open Publications Nos. 4-297023 and 7-312350. According to this technique, an amorphous or polycrystalline nitride semiconductor layer (i.e., a GaN or GalaAlaN (where $0<a\leqq 1$) layer) is once formed on a single crystal substrate of sapphire or silicon at a relatively low temperature by an MOVPE process. Thereafter, the nitride semiconductor layer is heated to form a partially single crystalline buffer layer and then nitride semiconductor layers for a semiconductor device are epitaxially grown on the buffer layer.

A light-emitting device disclosed in Japanese Laid-Open Publication No. 6-177423 is known as an exemplary semiconductor device using a nitride semiconductor layer formed on a buffer layer. As shown in FIG. **14**, this light*emitting device **900** includes: a buffer layer **95** of polycrystalline or amorphous GaN or $Ga_{1-a}Al_aN$ (where $0<a\leqq 1$); an n-type $Ga_{1-b}Al_bN$ (where $0\leqq b<1$) cladding layer **96**; an n-type $In_xGa_{1-x}N$ (where $0<x<0.5$) active layer **97**; and a p-type $Ga_{1-c}Al_cN$ (where $0\leqq c<1$) cladding layer **98**, which are stacked in this order on a sapphire substrate **92**.

The crystal growing technique for the buffer layer **95** is also disclosed in Japanese Laid-Open Publications Nos. 4-297023 and 7-312350 identified above. Specifically, according to the method disclosed in these references, GaN or $Ga_{1-a}Al_aN$ (where $0<a\leqq 1$) crystals are grown at a temperature ranging from 200° C. to 900° C., both inclusive, by an MOVPE process to form the buffer layer **95**. In accordance with this method, part of the buffer layer **95** is turned into single crystals during a process of raising the temperature after the buffer layer **95** of polycrystalline $Ga_{1-a}Al_aN$ (where $0<a\leqq 1$) has been deposited on the sapphire substrate **92** at a low temperature and before a nitride semiconductor crystal layer, e.g., the n**15** type $Ga_{1-b}Al_bN$ (where $0\leqq b<1$) cladding layer **96**, is deposited at a temperature of about 1000° C.

The present inventors minutely analyzed the cross-section of nitride semiconductor crystals, which had been grown on a sapphire substrate at a low temperature by the conventional technique, using a transmission electron microscope. As a result, we found that the nitride semiconductor crystal layer, which had been formed by the prior art crystal growing technique, had a lot of dislocations and that the lifetime of a semiconductor device including such a nitride semiconductor layer was short.

In the conventional method for fabricating a semiconductor device, it seems to be only a small region of the buffer layer **95** within a plane of the sapphire substrate **92** that is turned into single crystals during the temperature raising process before the nitride semiconductor crystal layers are grown. Thus, it is considered that, in the remaining region of the buffer layer **95** that is not turned into single crystals, the polycrystals have poorly aligned orientations to generate a large number of dislocations (or other defects) in the interface between the sapphire substrate **92** and the buffer layer **95**. And such dislocations would grow to reach the nitride semiconductor crystal layers (i.e., the cladding layer **96**, active layer **97** and cladding layer **98** in this case). We found that the density of dislocations in the nitride semiconductor crystal layers was as high as 10^9 cm^{-2}, thus adversely shortening the life of the semiconductor device.

Still another technique of forming an AlN buffer layer by nitrifying (in this specification, to "nitrify" means "to combine with nitrogen or its compounds") the surface of a sapphire single crystal substrate was suggested in Japanese Laid-Open Publication No. 63-178516, for example. In accordance with this technique, however, the buffer layer is also likely to crack or a lot of dislocations are also created in the buffer layer as in the prior art method just described. Thus, this technique has not been put into practice, either.

SUMMARY OF THE INVENTION

An object of the present invention is providing a method for growing nitride semiconductor crystals with the number of dislocations created in a nitride semiconductor crystal layer reduced, a highly reliable semiconductor device with a longer lifetime, and a method for fabricating the same.

A method for growing nitride semiconductor crystals according to the present invention includes the steps of: a) forming a first metal single crystal layer on a substrate; b) forming a metal nitride single crystal layer by nitrifying the first metal single crystal layer; and c) epitaxially growing a first nitride semiconductor layer on the metal nitride single crystal layer.

The present invention also provides a method for fabricating a nitride semiconductor device including a semiconductor multilayer structure and a pair of electrodes for applying a voltage to the semiconductor multilayer structure. In this method, the step of forming the semiconductor multilayer structure includes the step of epitaxially growing the first nitride semiconductor layer by the method of the present invention for growing nitride semiconductor crystals.

A nitride semiconductor device according to the present invention includes: a single crystal substrate; a metal nitride single crystal layer formed by nitrifying a metal single crystal layer on the single crystal substrate; a semiconductor multilayer structure including a first nitride semiconductor layer epitaxially grown on the metal nitride single crystal layer; and a pair of electrodes for applying a voltage to the semiconductor multilayer structure.

Another nitride semiconductor device according to the present invention includes: a single crystal substrate with conductivity; a metal nitride single crystal layer formed by nitrifying a metal single crystal layer on the single crystal substrate: a semiconductor multilayer structure including a first nitride semiconductor layer epitaxially grown on the metal nitride single crystal layer; and a pair of electrodes formed to face each other on respective surfaces of the single crystal substrate and the semiconductor multilayer structure, which are interposed between the surfaces.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1**A, **1**B and **1**C are cross-sectional views illustrating a method for growing nitride semiconductor crystals according to an exemplary embodiment of the present invention.

FIGS. **2**A, **2**B and **2**C are cross-sectional views illustrating a method for growing nitride semiconductor crystals according to another embodiment of the present invention.

FIGS. **3**A, **3**B and **3**C are cross-sectional views illustrating a method for growing nitride semiconductor crystals according to still another embodiment of the present invention.

FIGS. **4**A, **4**B and **4**C are cross-sectional views illustrating a method for growing nitride semiconductor crystals according to yet another embodiment of the present invention.

FIGS. **5**A, **5**B, **5**C and **5**D are cross-sectional views illustrating a method for growing nitride semiconductor crystals according to yet another embodiment of the present invention.

FIGS. **6**A, **6**B, **6**C and **6**D are cross-sectional views illustrating a method for growing nitride semiconductor crystals according to yet another embodiment of the present invention.

FIG. **7** is a cross-sectional view schematically illustrating a light-emitting device **100** in a first specific example of a first embodiment according to the present invention.

FIGS. **8**A, **8**B and **8**C are cross-sectional views schematically illustrating a method for fabricating the light-emitting device **100** shown in FIG. **7**.

FIG. **9** is a graph illustrating respective relationships between operating time and variation in operating current for the light-emitting devices of the present invention and a conventional light-emitting device.

FIG. **10** is a cross-sectional view schematically illustrating a light-emitting device **200** in a first specific example of a second embodiment according to the present invention.

FIGS. **11**A, **11**B and **11**C are cross-sectional views schematically illustrating a method for fabricating the light-emitting device **200** shown in FIG. **10**.

FIG. **12** is a cross-sectional view schematically illustrating a light-emitting device **300** in a second specific example of the second embodiment according to the present invention.

FIG. **13** is a cross-sectional view schematically illustrating a light-emitting device **400** in a third specific example of the second embodiment according to the present invention.

FIG. **14** is a cross-sectional view schematically illustrating a conventional light-emitting device.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a method for growing nitride semiconductor crystals according to the present invention, first, a metal single crystal layer is formed on a substrate, and then a metal nitride single crystal layer is formed by nitrifying the metal single crystal layer. Thereafter, nitride semiconductor layers are epitaxially grown on the resulting metal nitride single crystal layer. In the nitrification process step, the metal single crystal layer need not be nitrified entirely. Alternatively, only part of the metal single crystal layer may be nitrified and then nitride semiconductor layers may be epitaxially grown on a metal nitride single crystal layer formed around the surface of the metal single crystal layer. As a further alternative, another metal single crystal layer, different from the metal single crystal layer to be nitrified, may be formed on the substrate and then the metal single crystal layer to be nitrified may be formed thereon.

The metal nitride single crystal layer, on which nitride semiconductor layers are to be epitaxially grown, functions as a conventional buffer layer, thus improving the crystallinity of the nitride semiconductor layers. Such a buffer layer, made of a metal nitride formed by nitrifying the metal single crystals, is a single crystal layer with a much smaller number of defects than a polycrystalline layer or layer formed by turning part of a polycrystalline layer into single crystals in the prior art. Accordingly, nitride semiconductor layers with a low density of dislocations may be deposited thereon by an epitaxy process.

In addition, compared to a conventional crystal-growing technique, the creation of cracks in the metal nitride single crystal layer or the nitride semiconductor layers formed thereon can be suppressed or virtually prevented. The creation of cracks can be suppressed probably by the following mechanism. Firstly, in accordance with the thermal hysteresis during the process steps of forming the metal single crystal layer and nitrifying the metal single crystal layer, thermal stress, which is caused between the metal nitride single crystal layer and the substrate or the metal single crystal layer can be reduced. Secondly, since the interfacial state between the metal single crystal layer or the metal nitride single crystal layer and the substrate is different from that resulting from the conventional technique, the stress can be relaxed, or the generation of the stress can be suppressed.

The metal single crystal layer may be formed by a known technique. For example, the metal single crystal layer may be epitaxially grown on a single crystal substrate by an ionized cluster beam (ICB) process or a sputtering technique. Methods for growing a metal single crystal layer by an ICB process, ICB apparatuses and growth conditions are disclosed, for example, by H. Inokawa et al., Jpn. J. Appl. Phys. 24 (1985), pp. L173–L174, I. Yamada et al., J. Appl. Phys. 56 (1986), pp. 2746–2750 and K. Yamada, edited by Japan Surface Science Association, "Thin-film Designing with Ion beams", Section 5.5, pp. 90–95, Kyoritsu Shuppan, 1991. A method for growing a metal single crystal layer by a sputtering technique is described, for example, by S. Yokoyama et al., Jpn. J. Appl. Phys. 32 (1993), pp. L283–L286. According to the ICB process, in particular, a metal single crystal layer of excellent quality can be formed (the interfacial state between the metal single crystal layer and the single crystal substrate would also be good). In addition, in accordance with the ICB process, a metal single crystal layer can be epitaxially grown on a single crystal substrate with a relatively large lattice mismatch (e.g., about 25% or more). The documents cited above are hereby incorporated by reference as those disclosing a method for epitaxially growing a metal single crystal layer, which is applicable to the embodiments of the present invention.

According to a method for epitaxially growing a metal single crystal layer on a single crystal substrate, various types of single crystal substrates may be used. The single crystal substrate may either be a dielectric (insulator) or have electrical conductivity (semiconductor or conductor). If a conductive substrate is used, then the structure of the semiconductor device can be advantageously simplified. This point will be detailed in describing embodiments of a method for fabricating a semiconductor device.

If a nitride semiconductor device is fabricated in accordance with the method for growing nitride semiconductor crystals according to the present invention, the creation of cracks in a nitride semiconductor layer can be suppressed and the density of defects in the layer can be reduced. Accordingly, a highly reliable nitride semiconductor device with a long lifetime can be fabricated.

Hereinafter, a method for growing nitride semiconductor crystals according to an exemplary embodiment of the present invention will be described with reference to FIGS. **1**A through **6**. In all the drawings referred to in the following description, components with similar basic functions will be identified by the same reference numeral for the sake of simplicity.

FIGS. **1**A, **1**B and **1**C are cross-sectional views illustrating respective process steps for growing nitride semiconductor crystals in an exemplary embodiment of the present invention.

First, as shown in FIG. **1**A, a metal single crystal layer **24** is formed on a substrate **22**. For example, a single crystal substrate is used as the substrate **22** and the metal single crystal layer **24** is epitaxially grown on the single crystal substrate **22** by an ICB process, which may be carried out as disclosed in the documents cited above. For instance, the ICB process may be performed at room temperature within an ambient at a pressure of about 1×10^{-9}Torr (i.e., about 1.4×10^{-7} Pa) or less. Before this epitaxial growth process step is performed, a process step of cleaning the surface of the single crystal substrate **22** may be carried out.

The single crystal substrate **22** may be made of: insulator single crystals of sapphire, spinel, magnesium oxide, zinc oxide, chromium oxide, lithium niobium oxide, lithium tantalum oxide or lithium gallium oxide; semiconductor single crystals represented by $\mathrm{Si}_{1-s-t}\mathrm{tGe}_s\mathrm{C}_t$ (where $0 \leq s, t \leq 1$ and $0 \leq s+t \leq 1$) or $A_{1-u}B_u$ (where $0<u<1$, A is one of Al, Ga and In and B is one of As, P and Sb); or metal single crystals of hafnium, for example. The metal single crystal layer **24** to be epitaxially grown on the single crystal substrate **22** may be made of $\mathrm{Al}_{1-x-y}\mathrm{Ga}_x\mathrm{In}_y$ (where $0 \leq x, y \leq 1$ and $0 \leq x+y<1$).

Next, as shown in FIG. **1**B, the metal single crystal layer **24** is nitrified, thereby forming the metal nitride single crystal layer **25**. This nitrification process step may be performed by heating the metal single crystal layer **24** within an ambient of a compound containing nitrogen. The compound containing nitrogen is preferably hydrazine (N_2H_4) or ammonium (NH_3). Hydrazine is particularly preferable, because hydrazine has higher nitrification ability than ammonium and can shorten the nitrification time or lower the nitrification temperature.

The nitrification temperature can be appropriately set depending on the necessity. However, the upper limit of the nitrification temperature is preferably lower than the melting point of the metal single crystal layer **24**. This is because if the metal single crystal layer **24** is heated at a temperature equal to or higher than the melting point thereof for a long time, then the metal single crystal layer **24** melts and the crystal structure thereof collapses. In such a situation, the metal nitride layer, formed by the nitrification, is sometimes a non-single crystal layer or a crystal layer with a large number of dislocations. Accordingly, in order to form a metal nitride single crystal layer of good quality, the metal single crystal layer is preferably nitrified at a temperature lower than the melting point of the metal single crystal layer by about 100° C. or more. The nitrification temperature has no particular lower limit. However, since the nitrification reaction of a metal is an Arrhenius-type reaction, the higher the nitrification temperature, the shorter the time taken to nitrify the metal single crystal layer. For example, in nitrifying a metal single crystal layer of $\mathrm{Al}_{1-x-y}\mathrm{Ga}_x\mathrm{In}_y$, the nitrification temperature is preferably about 200° C. or more within the hydrazine ambient or about 400° C. or more within the ammonium ambient. If the nitrification temperature is set at such a value, a metal single crystal layer with a thickness of several tens nanometers can be nitrified within several tens minutes. Since the metal nitride single crystal layer **25**, which is formed by nitrifying the metal single crystal layer **24**, is thicker than the original metal single crystal layer **24**, the thickness of the layer **25** is emphasized in FIG. **1**B.

Then, a nitride semiconductor layer **26** is epitaxially grown on the resulting metal nitride layer **25** by a known technique. For example, a layer made of a nitride represented as $\mathrm{Al}_{1-s-t}\mathrm{Ga}_s\mathrm{In}_t\mathrm{N}$ (where $0 \leq s, t \leq 1$ and $0 \leq s+t \leq 1$) may be epitaxially grown as the nitride semiconductor layer **26**. Naturally, the composition of the nitride semiconductor layer **26** may be different from that of the metal nitride layer **25**. Since the metal nitride single crystal layer **25** has a small number of dislocations, the nitride semiconductor layer **26**, which is epitaxially grown thereon, is also a single crystal layer with a small number of dislocations. In addition, compared to a conventional crystal-growing technique, the creation of cracks in the metal nitride single crystal layer **25** or the nitride semiconductor layer **26** formed thereon can be suppressed or virtually prevented. For example, according to the conventional crystal-growing technique, if a GaN layer is epitaxially grown on an AlN buffer layer deposited on an Si single crystal substrate at a high temperature (e.g., about 1000° C.), a distance between cracks, which are generated in the AlN buffer layer and the GaN layer, is about 20 μm on average. On the other hand, if the GaN layer is epitaxially grown on an AlN layer obtained by nitrifying an Al metal single crystal layer, a distance between cracks is about 2 mm to 30 mm on average. An average distance between cracks, which are generated in the nitride semiconductor layer formed according to the crystal-growing method of the present invention, is about 10 mm or more. Therefore, according to the crystal-growing method of the present invention, semiconductor devices can be fabricated with a good yield.

Another exemplary embodiment of a method for growing nitride semiconductor crystals is illustrated in FIGS. **2**A, **2**B and **2**C. This embodiment is different from the embodiment shown in FIGS. **1**A, **1**B and **1**C in the nitrification process step shown in FIG. **2**B. Specifically, in the step shown in FIG. **2**B, the metal single crystal layer **24** is nitrified and metal atoms diffuse from the metal single crystal layer **24** into the substrate **22** to form a metal diffused layer **22***a* within the surface of the substrate **22** (i.e., the interface between the metal nitride single crystal layer **25** and the substrate **22**).

The probability of diffusion of the metal atoms is dependent on the combination of materials for the single crystal substrate **22** and the metal single crystal layer **24**. For example, if the single crystal substrate **22** is made of silicon or a semiconductor represented as $A_{1-u}B_u$ (where $0<u<1$, A is one of Al, Ga and In and B is one of As, P and Sb) and the metal single crystal layer **24** is made of Al or an alloy containing Al, more specifically, $Al_{1-x-y}Ga_xIn_y$, then Al atoms are likely to diffuse into the substrate **22** to form the metal diffused layer **22***a* easily. For example, if Al is used to form the metal single crystal layer **24** and the resultant Al single crystal layer is nitrified at about 550° C. for about an hour, then a metal diffused layer **22***a* with a thickness of about 1 nm is obtained.

It is considered that this metal diffused layer **22***a* improves the adhesion between the substrate **22** and the metal nitride single crystal layer **25** and relaxes a stress resulting from a difference in thermal expansion coefficient therebetween. In addition, the metal diffused layer **22***a* can also reduce the thermal contact resistance between the substrate **22** and the multilayer structure formed thereon. Furthermore, when the single crystal substrate **22** and the metal nitride single crystal layer **25** both have conductivity, the metal diffused layer **22***a* can constitute an ohmic contact therebetween.

Still another exemplary embodiment of a method for growing nitride semiconductor crystals is illustrated in FIGS. **3**A, **3**B and **3**C. This embodiment is different from the embodiment shown in FIGS. **1**A, **1**B and **1**C in the nitrification process step shown in FIG. **3**B. Specifically, in the step shown in FIG. **3**B, only a part of the metal single crystal layer **24** is nitrified to form the metal nitride single crystal layer **25**. The thickness of that part of the metal single crystal layer **24** to be nitrified can be controlled by adjusting the nitrification time, for example.

By partially leaving the metal single crystals **24** between the single crystal substrate **22** and the metal nitride single crystal layer **25** without completely nitrifying the metal single crystal layer **24**, the thermal contact resistance between the substrate **22** and the multilayer structure formed thereon can be reduced. In addition, a stress created between the single crystal substrate **22** and the metal nitride single crystal layer **25** can be relaxed by the metal single crystal layer **24**. This is probably because the elastic modulus of a metal is generally lower than that of a nitride of the metal.

Yet another exemplary embodiment of a method for growing nitride semiconductor crystals is illustrated in FIGS. **4**A, **4**B and **4**C. This embodiment is different from the embodiment shown in FIGS. **1**A, **1**B and **1**C in the nitrification process step shown in FIG. **4**B. Specifically, in the step shown in FIG. **4**B, only a part of the metal single crystal layer **24** is nitrified to form the metal nitride single crystal layer **25**, and metal atoms diffuse from the metal single crystal layer **24** into the substrate **22** to form a metal diffused layer **22***a* within the surface of the substrate **22** (i.e., the interface between the metal single crystal layer **24** and the substrate **22**). As already described for the embodiment shown in FIGS. **2**A, **2**B and **2**C, the metal diffused layer **22***a* is formed sometimes easily but sometimes not, dependent on the combination of materials for the single crystal substrate **22** and the metal single crystal layer **24**. By using the above-exemplified combination of materials and controlling the thickness of that part of the metal single crystal layer **24** to be nitrified, the structure shown in FIG. **4**B can be obtained. As already described for the embodiment shown in FIGS. **3**A, **3**B and **3**C, the thickness of that part of the metal single crystal layer **24** to be nitrified can be controlled by adjusting the nitrification time, for example.

Yet another exemplary embodiment of a method for growing nitride semiconductor crystals is illustrated in FIGS. **5**A, **5**B, **5**C and **5**D. This embodiment is different from the foregoing embodiments in that an additional metal single crystal layer **23** is formed before the metal single crystal layer **24** to be nitrified is formed over the substrate **22** as shown in FIG. **5**A.

The metal single crystal layer **23**, as well as the metal single crystal layer **24** of the foregoing embodiments, may be formed by a known technique. For example, a single crystal substrate is prepared as the substrate **22** and the metal single crystal layer **23** is epitaxially grown thereon by an ICB process, for example. A metal material for the metal single crystal layer **23** is preferably Au or an alloy containing Au (e.g., an alloy of Au and Ge). By forming this additional metal single crystal layer **23**, the thermal contact resistance between the substrate **22** and the multilayer structure formed thereon can be reduced.

If the single crystal substrate **22** is made of a semiconductor represented as $Si_{1-s-t}Ge_sC_t$ (where $0 \leqq s$, $t \leqq 1$ and $0 \leqq s+t \leqq 1$) or $A_{1-u}B_u$ (where $0<u<1$, A is one of Al, Ga and In and B is one of As, P and Sb) where the metal single crystal layer **23** is made of Au or an alloy containing Au, then metal atoms constituting the metal single crystal layer **23** diffuse into the single crystal substrate **22** to form a metal diffused layer therein during the process step of nitrifying the metal single crystal layer **24**. As a result, not only thermal contact resistance but also electrical contact resistance can be reduced between the single crystal substrate **22** and the semiconductor multilayer structure formed thereon. In this case, part of the atoms constituting the metal single crystal layer **23** may be diffused. Alternatively, as shown in FIGS. **6**A, **6**B, **6**C and **6**D, a metal diffused layer **22***a* may be formed by diffusing all the atoms constituting the metal single crystal layer **23** into the single crystal substrate **22** during the step of forming the metal nitride single crystal layer **25** through the nitrification of the metal single crystal layer **24**. According to this method, the metal single crystal layer **23** disappears (see FIG. **6**C). In order to eliminate the metal single crystal layer **23** through diffusion, the thickness of the metal single crystal layer **23** is preferably about 3 nm or less. Also, the temperature and time for the process step of nitrifying the metal single crystal layer **24** may be set based on the degree of diffusion of the metal single crystal layer **23**. For example, if atoms in the metal single crystal layer **23** should be continuously diffused after the nitrification reaction of the metal single crystal layer **24** is over, heating may be continued.

This embodiment may be combined with any of the foregoing embodiments. For example, if the metal single crystal layer **23** is made of Au or an alloy containing Au and the single crystal substrate **22** is made of a semiconductor represented as $Si_{1-s-t}Ge_sC_t$ or $A_{1-u}B_u$, then metal atoms diffuse from the metal single crystal layer **23** into the single crystal substrate **22** to form the metal diffused layer **22***a* as in the embodiment shown in FIG. **2**B. In this case, if the metal single crystal layer **23** is sufficiently thin (e.g., about 3 nm or less), then all the metal atoms constituting the metal single crystal layer **23** diffuse into the single crystal substrate **22** and substantially no metal single crystal layer **23** is left. In this structure, the AlN single crystal layer **25** with satisfactorily aligned crystal orientations is formed on the sapphire substrate **22**. Accordingly, the density of defects or dislocations can be reduced both in the interface between the sapphire substrate **22** and the AlN single crystal layer **25** and in the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked thereon. In this structure, increase in resistance due to a Schottky barrier generated by a semiconductor/metal interface can be prevented, since there is no semiconductor/metal interface.

Also, after the metal single crystal layers **23** and **24** have been formed, only a part of the metal single crystal layer **24** may be nitrified as described for the embodiment shown in FIG. **3**B. Furthermore, after the metal single crystal layers **23** and **24** have been formed, the metal diffused layer **22***a* may be formed and only a part of the metal single crystal layer **24** may be nitrified to leave the metal single crystal layer **24** between the metal nitride single crystal layer **25** and the metal single crystal layer **23** as described for the embodiment shown in FIG. **4**B. In any combination, the effects of the embodiment shown in FIG. **2**B, **3**B or **4**B can be additionally attained.

Since a nitride semiconductor layer having (0001) principal surface is generally used in a semiconductor device, it is preferable to form a metal nitride layer having (0001) principal surface so that a nitride semiconductor layer having (0001) principal surface can be epitaxially grown on the metal nitride layer. More specifically, when a single crystal substrate, made of semiconductor single crystals represented by $Si_{1-s-t}Ge_sC_t$ (where $0 \leqq s, t \leqq 1$ and $0 \leqq s+t \leqq 1$) or $A_{1-u}B_u$ (where $0<u<1$, A is one of Al, Ga and In and B is one of As, P and Sb), is used, an Al (where $0 \leqq x, y \leqq 1$ and $0 \leqq x+y<1$) single crystal layer having (0001) principal surface can be obtained by nitrifying an $Al_{1-x-y}Ga_xIn_y$ layer having (111) principal surface epitaxially grown on (111) plane of the single crystal substrate made of $Si_{1-s-t}Ge_sC_t$ or $A_{1-u}B_u$.

Hereinafter, specific embodiments of fabricating a semiconductor device in accordance with the foregoing method for growing nitride semiconductor crystals will be described. In the following illustrative embodiments, a light-emitting device (i.e., a semiconductor laser diode) is fabricated as an exemplary semiconductor device. However, the present invention is not limited to those specific embodiments, but is applicable to various other semiconductor devices like a field effect transistor (FET).

Embodiment 1

In a first exemplary embodiment of the present invention, a light-emitting device **100** is formed using a substrate with no conductivity.

SPECIFIC EXAMPLE 1-1

As shown in FIG. **7**, the light-emitting device **100** includes: an AlN single crystal layer **25** (thickness: 10 nm); an n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26** (thickness: 1 μm); a multiple quantum well (MQW) active layer **27**; a p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** (thickness: 0.5 μm); and a p-type GaN contact layer **29** (thickness: 0.1 μm), which are stacked in this order on a sapphire substrate **22**. The MQW active layer **27** is formed by alternately stacking ten pairs of undoped $In_{0.2}Ga_{0.8}N$ layers (thickness: 5 nm) and undoped GaN layers (thickness: 5 nm). Of these layers, the lowermost undoped GaN layer is in contact with the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**.

This semiconductor multilayer structure, including the cladding layer **26**, active layer **27**, cladding layer **28** and contact layer **29**, which are formed on the AlN single crystal layer **25** has been subjected to a mesa-etching process. Through this etching process, a pair of electrodes **32***a* and **32***b* for applying a voltage to the semiconductor multilayer structure are formed on the contact layer **29** and on the cladding layer **26**, respectively.

In this structure, the AlN single crystal layer **25** with satisfactorily aligned crystal orientations is formed on the sapphire substrate **22**. Accordingly, the density of defects or dislocations can be reduced both in the interface between the sapphire substrate **22** and the AlN single crystal layer **25** and in the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked thereon.

The light-emitting device **100** may be fabricated in accordance with the crystal-growing method shown in FIGS. **1**A through **1**C. A method for fabricating this light-emitting device **100** will be described with reference to FIGS. **8**A, **8**B and **8**C.

First, as shown in FIG. **8**A, an Al single crystal layer **24** is deposited on a sapphire substrate **22** by an ICB process. Next, as shown in FIG. **8**B, the Al single crystal layer **24** is nitrified to be an AlN single crystal layer **25**. The nitrification may be performed by reacting nitrogen components, which are included in a nitrogen compound such as hydrazine or ammonium contained in an appropriate carrier gas (e.g., H_2 gas), with the Al single crystal layer **24** while the temperature of the sapphire substrate **22** is kept at 550° C., which is about 100° C. lower than the melting point of Al single crystals (i.e., 660° C.).

Thereafter, as shown in FIG. **8**C, an n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26** doped with Si, an MQW active layer **27**, a p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** doped with Mg and a p-type GaN contact layer **29** doped with Mg are stacked in this order on the AlN single crystal layer **25** by an MOVPE process. In this process step, crystals for the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29** are grown at 1000° C. while crystals for the MQW active layer **27** are grown at 800°C.

The resulting semiconductor multilayer structure, including the respective layers **26**, **27**, **28** and **29**, is partially etched, thereby exposing the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**. Finally, respective ohmic electrodes **32***a* and **32***b* are formed on the p-type GaN contact layer **29** and on the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26** to complete the light-emitting device **100**. The electrode **32***a* may be formed of, for example, Ni/Au, and the electrode **32***b* may be formed of, for example, Ti/Au by an electron beam deposition method.

In this structure, since the AlN single crystal layer **25** is formed by nitrifying the Al single crystal layer **24**, the AlN single crystal layer **25** can be formed over the entire surface of the sapphire substrate **22**. Accordingly, the crystallinity of the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked on the AlN single crystal layer **25**, can be improved.

The cross section of the light-emitting device **100** according to the first specific example of the first embodiment was observed with a transmission electron microscope (TEM). As a result, the density of defects or dislocations in the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and GaN contact layer **29** was $1.0 \times 10^5/cm^2$, which is about 1/10,000 compared to a conventional light-emitting device.

SPECIFIC EXAMPLE 1-2

A light-emitting device according to a second specific example of the first embodiment includes an $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** (thickness: 5 nm), the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked in this order on an $MgAl_2O_4$ (spinel) substrate **22** as shown in FIG. **7**.

In this structure, the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** with satisfactorily aligned crystal orientations is formed on the spinel substrate **22**. Accordingly, the density of defects or dislocations can be reduced in both the interface between the spinel substrate **22** and the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25**, and the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**. MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked thereon.

A method for fabricating this light-emitting device **100** will be described with reference to FIGS. **8**A, **8**B and **8**C again.

First, as shown in FIG. **8**A, an $Al_{0.9}Ga_{0.1}$ alloy single crystal layer **24** is deposited to be 5 nm thick on a spinel substrate **22** by an ICB process. Next, as shown in FIG. **8**B, the $Al_{0.9}Ga_{0.1}$ alloy single crystal layer **24** is nitrified to be an $Al_{0.9}Ga_{0.1}N$ single crystal layer **25**. The nitrification may be performed by reacting nitrogen components, which are included in a nitrogen compound such as hydrazine or ammonium contained in an appropriate carrier gas (e.g., H_2 gas), with the $Al_{0.9}Ga_{0.1}$ alloy single crystal layer **24** while the temperature of the spinel substrate **22** is kept at 500° C.

Thereafter, as shown in FIG. **8**C, n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26** doped with Si, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** doped with Mg and p-type GaN contact layer **29** doped with Mg are stacked in this order on the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** as in the first specific example. The resulting semiconductor multilayer structure, including the respective layers **26**, **27**, **28** and **29**, is partially etched, thereby exposing the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**. Finally, respective ohmic electrodes **32***a* and **32***b* are formed on the p-type GaN contact layer **29** and on the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**.

In this structure, since the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** is formed by nitrifying the $Al_{0.9}Ga_{0.1}$ alloy single crystal layer **24**, the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** can be formed over the entire surface of the spinel substrate **22**. Accordingly, the crystallinity of the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked on the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25**, can be improved.

The cross section of the light-emitting device **100** according to the second specific example of the first embodiment was observed with a TEM. As a result, the density of defects or dislocations in the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and GaN contact layer **29** was $1.0\times10^5/cm^2$, which is about $\frac{1}{10,000}$ compared to a conventional light-emitting device.

FIG. **9** illustrates respective lifetimes of the light-emitting devices **100** according to the first and second specific examples of the first embodiment (hereinafter, identified by E**1** and E**2**, respectively) and a conventional light-emitting device C, which are all operated at a temperature of 70° C. with an optical output of 5 mW. In FIG. **9**, the curves E**1**, E**2** and C indicate respective relationships between the operating time and a variation in operating current per unit time of the light-emitting devices E**1**, E**2** and C. In FIG. **9**, as the variation $\Delta I/\Delta t$, which is a variation of the operating current with the operating time, comes closer to 1, a light-emitting device deteriorates to a lesser degree and can operate for a longer time. As shown in FIG. **9**, in the light-emitting devices E**1** and E**2** of the present invention, $\Delta I/\Delta t$ is still close to 1 even after these devices have been operated for 10,000 hours. In contrast, after the conventional light-emitting device C has been operated for 5,000 hours, $\Delta I/\Delta t$ greatly deviates from 1. Accordingly, the light-emitting devices E**1** and E**2** of the present invention have much longer lifetimes, and are a lot more reliable, than the conventional light-emitting device C. It should be noted that the oscillation wavelengths of these light-emitting devices were all 420 nm.

In the foregoing specific examples, the same effects can be attained if the sapphire or spinel substrate **22** is replaced with a single crystal substrate of MgO, ZnO, Cr_2O_3, $LiNbO_3$, $LiTaO_3$ or $LiGaO_2$.

As described above, the first embodiment of the present invention provides a semiconductor device with reduced defects or dislocations in the interface between an insulating single crystal substrate and a nitride semiconductor crystal layer, a longer lifetime and higher reliability and a method for fabricating the same.

In the foregoing illustrative embodiment, a method for fabricating a light-emitting device in accordance with the nitride semiconductor crystal-growing method shown in FIGS. **1**A through **1**C has been described. Alternatively, any of the other crystal-growing methods shown in FIGS. **2**A through **6**D is also applicable. According to any of these methods, the same effects as those of the first embodiment can be attained.

Embodiment 2

In a second exemplary embodiment of the present invention, a light-emitting device **200** is formed using a substrate with conductivity, which includes a semiconductor substrate and a conductor substrate made of a metal, for example.

SPECIFIC EXAMPLE 2-1

As shown in FIG. **10**, the light-emitting device **200** according to a first specific example of the second embodiment includes: an Al single crystal layer **24** (thickness: 8 nm); an AlN single crystal layer **25** (thickness: 2 nm); an n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26** (thickness: 1 μm); an MQW active layer **27**; a p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** (thickness: 0.5 μm); and a p-type GaN contact layer **29** (thickness: 0.1 μtm), which are stacked in this order on an n-type Si substrate **22**. The MQW active layer **27** is formed by alternately stacking twenty pairs of undoped $In_{0.9}Ga_{0.1}N$ layers (thickness: 5 nm) and undoped GaN layers (thickness: 5 nm). Of these layers, the lowermost undoped GaN layer is in contact with the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**.

A pair of electrodes **32***a* and **32***b* for applying a voltage to the semiconductor multilayer structure, including the n-type cladding layer **26**, active layer **27**, p-type cladding layer **28** and contact layer **29**, which are formed on the AlN single crystal layer **25**, are formed on the contact layer **29** and on the Si single crystal substrate **22**, respectively, so as to face each other.

In this structure, the Al single crystal layer **24** with satisfactorily aligned crystal orientations is formed on the n-type Si single crystal substrate **22**, and the AlN single crystal layer **25** is formed thereon. Accordingly, the density of defects or dislocations can be reduced in both the interface between the n-type Si single crystal substrate **22** and the Al single crystal layer **24**, and the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked thereon. Also, heat generated in the MQW active layer **27** can be directly dissipated through the n-type Si single crystal substrate **22**. Furthermore, since an electrode can be formed on the back of the n-type Si single crystal substrate **22**, an increased number of light-emitting devices can be formed per substrate **22** compared to a conventional structure. That is to say, a light-emitting device can be fabricated at a lower cost.

The light-emitting device **200** may be fabricated in accordance with the crystal-growing method shown in FIGS. **3**A through **3**C. A method for fabricating this light-emitting device **200** will be described with reference to FIGS. **11**A, **11**B and **11**C.

First, as shown in FIG. **11**A, an Al single crystal layer **24** is deposited to be 10 nm thick on an n-type Si single crystal substrate **22** by an ICB process. Next, as shown in FIG. **8**B, part of the Al single crystal layer **24** is nitrified to the depth of 2 nm as measured from the surface thereof, thereby turning that part into an AlN single crystal layer **25** with the thickness of 2 nm. The nitrification may be performed by reacting nitrogen components, which are included in a nitrogen compound such as hydrazine or ammonium contained in an appropriate carrier gas (e.g., H_2 gas), with the Al single crystal layer **24** while the temperature of the n-type Si single crystal substrate **22** is kept at 550° C., which is about 100° C. lower than the melting point of Al single crystals (i.e., 660° C.).

Thereafter, as shown in FIG. **1**C, n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26** doped with Si, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** doped with Mg and p-type GaN contact layer **29** doped with Mg are stacked in this order on the AlN single crystal layer **25** by an MOVPE process. In this process step, crystals for the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29** are grown at 1000° C., while crystals for the MQW active layer **27** are grown at 800° C.

Finally, respective ohmic electrodes **32***a* and **32***b* are formed to face each other on the p-type GaN contact layer **29** and on the n-type Si single crystal substrate **22**, thereby completing the light-emitting device **200**. The ohmic electrode **32***b* may be formed of, for example, Al, Ti or Pt, with an optional annealing step at about 300° C. to about 400° C. The ohmic electrode **32***b* may be formed as described in Embodiment 1 of the present invention.

In this structure, since the AlN single crystal layer **25** is formed by nitrifying the Al single crystal layer **24**, the Al and AlN single crystal layers **24** and **25** can be formed over the entire surface of the n-type Si single crystal substrate **22**. Accordingly, the crystallinity of the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked on the AlN single crystal layer **25**, can be improved.

The cross section of the light-emitting device **200** according to the first specific example of the second embodiment was observed with a TEM. As a result, the density of defects or dislocations in the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29** was $1.0\times10^5/cm^2$, which is about 1/10,000 compared to a conventional light-emitting device.

SPECIFIC EXAMPLE 2-2

A light-emitting device **300** according to a second specific example of the second embodiment includes $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** (thickness: 5 nm), n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked in this order on an n-type GaAs substrate **22** as shown in FIG. **12**.

In this structure, the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** with satisfactorily aligned crystal orientations is formed on the n-type GaAs substrate **22**. Accordingly, the density of defects or dislocations can be reduced in both the interface between the n-type GaAs substrate **22** and the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** and the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked thereon. Also, heat generated in the MQW active layer **27** can be directly dissipated through the n-type GaAs substrate **22**. Furthermore, since an electrode can be formed on the back of the n-type GaAs substrate **22**, an increased number of light-emitting devices can be formed per substrate **22** compared to a conventional structure. That is to say, a light-emitting device can be fabricated at a lower cost.

The light-emitting device **300** is fabricated in accordance with the crystal-growing method shown in FIGS. **1**A through **1**C. A method for fabricating this light-emitting device **300** will be described with reference to FIGS. **8**A, **8**B and **8**C again.

First, as shown in FIG. **8**A, an $Al_{0.9}Ga_{0.1}$ alloy single crystal layer **24** is deposited to be 5 nm thick on an n-type GaAs substrate **22** by an ICB process. Next, as shown in FIG. **8**B, the $Al_{0.9}Ga_{0.1}$ alloy single crystal layer **24** is nitrified to be an $Al_{0.9}Ga_{0.1}N$ single crystal layer **25**. The nitrification may be performed by reacting nitrogen components, which are included in a nitrogen compound such as hydrazine or ammonium contained in an appropriate carrier gas (e.g., H_2 gas), with the $Al_{0.9}Ga_{0.1}$ alloy single crystal layer **24** while the temperature of the n-type GaAs substrate **22** is kept at 500° C. Thereafter, as shown in FIG. **8**C, n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26** doped with Si, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** doped with Mg and p-type GaN contact layer **29** doped with Mg are stacked in this order on the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** as in the first specific example.

Finally, respective ohmic electrodes **32***a* and **32***b* are formed to each face other on the p-type GaN contact layer **29** and the n-type GaAs substrate **22**, thereby completing the light-emitting device **300**.

In this structure, since the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** is formed by nitrifying the $Al_{0.9}Ga_{0.1}$ alloy single crystal layer **24**, the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25** can be formed over the entire surface of the n-type GaAs substrate **22**. Accordingly, the crystallinity of the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked on the $Al_{0.9}Ga_{0.1}N$ single crystal layer **25**, can be improved.

The cross section of the light-emitting device **300** according to the second specific example of the second embodiment was observed with a TEM. As a result, the density of defects or dislocations in the n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and GaN contact layer **29** was $1.0\times10^5/cm^2$, which is about 1/10,000 compared to a conventional light-emitting device.

Respective lifetimes of the light-emitting devices **200** and **300** according to the first and second specific examples of the second embodiment, which were both operated at a temperature of 70° C. with an optical output of 5 mW, are substantially the same as those of the light-emitting devices E1 and E2 shown in FIG. **9**. That is to say, in the light-emitting devices **200** and **300** of the second embodiment, $\Delta I/\Delta t$ is still close to 1 even after these devices have been operated for 10,000 hours. In contrast, after the conventional light-emitting device C has been operated for 5,000 hours, $\Delta I/\Delta t$ greatly deviates from 1. Accordingly, the light-emitting devices **200** and **300** of the second embodiment also have much longer lifetimes, and are a lot more reliable, than the conventional light-emitting device C. It should be noted that the oscillation wavelengths of these light-emitting devices were all 420 nm.

In the foregoing specific examples of the second embodiment, the same effects are attained if the n-type Si single crystal substrate or n-type GaAs substrate **22** is replaced with a semiconductor single crystal substrate with conductivity such as n-type GaAs substrate or n-type SiC substrate. Also, a p-type semiconductor single crystal substrate with conductivity or a conductor single crystal substrate made of a metal such as hafnium may be used instead. Among various metals, hafnium single crystals are preferable, because the lattice constant of hafnium single crystals is close to that of nitride semiconductor single crystals.

As described above, according to the second embodiment of the present invention, a metal single crystal layer and a nitride semiconductor single crystal layer are formed in this order on a conductive single crystal substrate and then semiconductor layers are formed thereon. Accordingly, heat radiation can be improved and the density of defects or dislocations in the semiconductor layers can be reduced. Furthermore, since an electrode can be formed on the back of the conductive single crystal substrate, semiconductor devices can be fabricated at a lower cost.

SPECIFIC EXAMPLE 2-3

A light-emitting device **400** according to a third specific example of the second embodiment includes AlN single crystal layer **25** (thickness: 5 nm), n-type $Ga_{0.9}Al_{0.1}N$ cladding layer **26**, MQW active layer **27**, p-type $Ga_{0.9}Al_{0.1}N$ cladding layer **28** and p-type GaN contact layer **29**, which are stacked in this order on an n-type GaAs substrate **22** as shown in FIG. **13**. In addition, a metal diffused layer **22***a* is formed within the n-type GaAs substrate **22** in the vicinity of the surface thereof closer to the AlN single crystal layer **25**. The metal diffused layer **22***a* is formed by diffusing an alloy containing Au.

A pair of electrodes **32***a* and **32***b* for applying a voltage to the semiconductor multilayer structure, including the n-type cladding layer **26**, active layer **27**, p-type cladding layer **28** and contact layer **29**, which are formed on the AlN single crystal layer **25**, are formed on the contact layer **29** and on the n-type GaAs substrate **22**, respectively, so as to face each other.

The light-emitting device **400** is fabricated in accordance with the crystal-growing method shown in FIGS. **6**A through **6**D.

First, an n-type GaAs single crystal substrate **22**, of which the principal surface is (111) plane, is prepared. On the (111) plane of the single crystal substrate **22**, a metal single crystal layer **23** of an Au/Ge alloy is epitaxially grown to be about 1 nm thick by an ICB process as shown in FIG. **6**A. The principal surface of the resulting AuGe single crystal layer **23** is also (111) plane.

Next, an Al single crystal layer **24** doped with Si at about 10^{18} cm^{-3} is epitaxially grown to be about 20 nm thick on the (111) plane of the AuGe single crystal layer **23** by an ICB process. The principal surface of the resulting Al single crystal layer **24** is also (111) plane.

In epitaxially growing the metal single crystal layers **23** and **24** by an ICB process, an ICB apparatus, which includes source gas supplies (i.e., AuGe and Si-doped Al source gas supplies) for supplying the respective sources for the metal single crystal layers **23** and **24** within a single chamber and can control the flow rates of these source gases from the source gas supplies using a shutter, for example, is preferably used. If such an ICB apparatus is used, a high-purity film can be deposited, since there is no need to take out the specimens from the chamber (i.e., without breaking the vacuum within the chamber or causing leakage). The epitaxy of the metal single crystal layers **23** and **24** by the ICB process may be performed at room temperature, for example.

Then, while the Al single crystal layer **24** is nitrified, AuGe atoms are diffused from the AuGe single crystal layer **23** into the n-type GaAs substrate **22**. In this process step, the GaAs single crystal substrate **22** is heated up to a temperature lower than the respective melting points of the GaAs single crystal substrate **22** itself and the Al single crystal layer **24** (e.g., 550° C.) and a nitrogen-containing compound gas is supplied into the chamber. The nitrogen-containing compound is preferably hydrazine or ammonium. In particular, since hydrazine has high nitrification ability, hydrazine is preferable in view of the productivity. This is because the nitrification time can be shortened and the nitrification temperature can be lowered in such a case. By nitrifying the Al single crystal layer **24** with a thickness of 20 nm for about 10 to about 15 minutes, the AlN single crystal layer **25** is formed. The principal surf ace of the resulting AlN single crystal layer **25** is (0001) plane. Since the thickness increases as a result of the nitrification, the AlN layer **25** is illustrated in FIG. **6**B as being thicker than the Al layer **24**. Also, in this process step, AuGe atoms diffuse into the n-type GaAs substrate **22** to form an AuGe diffused layer **22***a* as shown in FIG. **6**C. To diffuse the AuGe atoms, the heating temperature and time may be adequately adjusted during the nitrification process step. Even after the nitrification reaction is substantially over, heating may be continued for the diffusion purpose only.

Thereafter, a cladding layer **26** of n-type $Ga_{0.9}Al_{0.1}N$ single crystals is epitaxially grown on the AlN single crystal layer **25** by an ICB process as shown in FIG. **6**D. Subsequently, a double heterojunction semiconductor multilayer structure, including the n-type cladding layer **26**, active layer **27**, p-type cladding layer **28** and contact layer **29**, is formed thereon by epitaxy as in the foregoing embodiments. And then electrodes **32***a* and **32***b* are formed to face each other on the contact layer **29** and on the n-type GaAs substrate **22**, respectively. As a result, the light-emitting device **400** shown in FIG. **13** is completed. The crystal structure of the semiconductor multilayer structure is hexagonal, and a laser device can be formed with crystals cleaved on the facets of the cavity.

In the AuGe diffused layer **22***a*, which is formed within the n-type GaAs substrate **22** in the vicinity of the surface thereof closer to the n-type AlN layer **25**, Ge atoms function as donors. Accordingly, the Ge atoms decrease the electrical resistance in the interface between the n-type GaAs substrate **22** and the n-type AlN layer **25**. Thus, this light-emitting device **400**, in which the pair of electrodes **32***a* and **32***b* are provided with the conductive substrate **22** and the semiconductor multilayer structure interposed therebetween, can have its operating voltage reduced.

In this third specific example of the second embodiment, if a p-type GaAs substrate is used as the conductive single crystal substrate **22** and AuNi single crystal layer and Mg-doped (e.g., about 0.5 mol %) Al single crystal layer are used as respective metal single crystal layers **23** and **24**, then a p-type AlN layer **25** can be formed over the p-type GaAs substrate **22**. Accordingly, a light-emitting device can be fabricated with a reversed arrangement of conductivity types in the double heterostructure. In this reversed arrangement, an AuNi diffused layer **22***a* is formed within the p-type GaAs substrate **22** in the vicinity of the surface thereof closer to the p-type AlN layer **25**. Ni atoms in the AuNi diffused layer **22***a* function as acceptors, thus decreasing the electrical resistance in the interface between the p-type GaAs substrate **22** and the p-type AlN layer **25**. As a result, the light-emitting device can operate at a lower voltage.

In this specific example, the metal single crystal layer **23** may be made of element Au or any other alloy containing Au.

According to the inventive method for growing nitride semiconductor crystals, a nitride semiconductor layer is epitaxially grown on a metal nitride single crystal layer obtained by nitrifying a metal single crystal layer. Therefore, a nitride semiconductor layer is obtained with a much smaller number of dislocations or defects than that formed by a conventional crystal growing method.

In addition, a highly reliable nitride semiconductor device with a longer lifetime can be obtained by fabricating the semiconductor device using the method for growing nitride semiconductor crystals according to the present invention. The inventive method for growing nitride semiconductor crystals is advantageously applicable to a method for fabricating a blue light emitting laser diode.

While the present invention has been described in a preferred embodiment, it will be apparent to those skilled in the art that the disclosed invention may be modified in numerous ways and may assume many embodiments other than that specifically set out and described above. Accordingly, it is intended by the appended claims to cover all modifications of the invention which fall within the true spirit and scope of the invention.

What is claimed is:

1. A method for growing nitride semiconductor crystals, comprising the steps of:

a) forming a first metal single crystal layer on a substrate;

b) forming a metal nitride single crystal layer by nitrifying the first metal single crystal layer; and

c) epitaxially growing a first nitride semiconductor layer on the metal nitride single crystal layer.

2. The method of claim **1**, wherein the step a) comprises the steps of:

i) providing a single crystal substrate; and

ii) epitaxially growing the first metal single crystal layer on the single crystal substrate.

3. The method of claim **2**, wherein the step ii) is performed by an ionized cluster beam process.

4. The method of claim **2**, wherein the first metal single crystal layer is made of $Al_{1-x-y}Ga_xIn_y$ (where $0 \leqq x, y \leqq 1$ and $0 \leqq x+y<1$).

5. The method of claim **4**, wherein the first nitride semiconductor layer is made of $Al_{1-s-t}Ga_sIn_tN$ (where $0 \leqq s, t \leqq 1$ and $0<s+t \leqq 1$).

6. The method of claim **2**, wherein in the step b), the first metal single crystal layer is nitrified within an ambient containing at least hydrazine or ammonium.

7. The method of claim **2**, wherein the step b) comprises the step of forming a metal diffused layer within the surface of the single crystal substrate by diffusing metal atoms from the first metal single crystal layer into the single crystal substrate.

8. The method of claim **2**, further comprising the step of forming a second metal single crystal layer on the single crystal substrate,

wherein in the step a), the first metal single crystal layer is epitaxially grown on the second metal single crystal layer.

9. The method of claim **8**, wherein the step b) comprises the step of forming a metal diffused layer within the surface of the single crystal substrate by diffusing metal atoms from the second metal single crystal layer into the single crystal substrate.

10. A method for fabricating a nitride semiconductor device, the device including a semiconductor multilayer structure and a pair of electrodes for applying a voltage to the semiconductor multilayer structure,

wherein the step of forming the semiconductor multi layer structure comprises the step of epitaxially growing the first nitride semiconductor layer by

a) forming a first metal single crystal layer on a substrate;

b) forming a metal nitride single crystal layer by nitrifying the first metal single crystal layer; and

c) epitaxially growing the first nitride semiconductor layer on the metal nitride single crystal layer.

11. The method of claim **10**, wherein the single crystal substrate has conductivity,

wherein in the step of forming the electrodes, the pair of electrodes are formed to face each other on respective surfaces of the single crystal substrate and the semiconductor multilayer structure, which are interposed between the surfaces.

12. The method of claim **10**, wherein the step of epitaxially growing the first nitride semiconductor layer comprises the steps of:

epitaxially growing the metal single crystal layer on a semiconductor single crystal substrate used as the single crystal substrate; and

forming the metal nitride single crystal layer by nitrifying the metal single crystal layer and forming a metal diffused layer within the surface of the semiconductor single crystal substrate by diffusing metal atoms from the metal single crystal layer into the semiconductor single crystal substrate.

13. The method of claim **12**, wherein the single crystal substrate is a single crystal substrate of silicon, the principal surface of which is (111) plane, and

wherein in the step of forming the metal single crystal layer, an $Al_{1-x-y}Ga_xIn_y$ (where $0 \leqq x, y \leqq 1$ and $0 \leqq x+y<1$) layer, of which the principal surface is also (111) plane, is epitaxially grown on the (111) plane of the single crystal substrate of silicon, and

wherein in the step of forming the metal nitride single crystal layer, the metal nitride single crystal layer of $Al_{1-x-y}Ga_xIn_y$ is formed to have a principal surface (0001) by nitrifying the metal single crystal layer of $Al_{1-x-y}Ga_xIn_y$.

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